

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Publication number:

**0 104 940****A1**

(12)

**EUROPEAN PATENT APPLICATION**

(21) Application number: 83305783.9

(22) Date of filing: 27.09.83

(51) Int. Cl.<sup>3</sup>: **C 07 D 291/06****C 07 D 419/04, C 07 D 419/10  
A 01 N 43/88, C 07 C 153/00**

(30) Priority: 28.09.82 US 425739

(43) Date of publication of application:  
04.04.84 Bulletin 84/14(84) Designated Contracting States:  
AT BE CH DE FR GB IT LI NL SE(71) Applicant: **UNIROYAL, INC.**  
1230 Avenue of the Americas Rockefeller Center  
New York, New York 10020(US)(71) Applicant: **UNIROYAL LIMITED**  
1500 Don Mills Road  
Don Mills Ontario M3B 3L4(CA)(72) Inventor: **Brouwer, Walter G.**  
15 Hickory Street  
Guelph Wellington Ontario N1G 2X2(CA)(72) Inventor: **Blem, Allen R.**  
812 Marion Road  
Cheshire New Haven Connecticut 06410(US)(72) Inventor: **Bell, Allyn R.**  
686 Wiese Road  
Cheshire New Haven Connecticut 06410(US)(72) Inventor: **Davis, Robert A.**  
1100 Notch Road  
Cheshire New Haven Connecticut 06410(US)(74) Representative: **Harrison, Michael Robert et al,**  
**URQUHART-DYKES & LORD** 11th Floor Tower House  
Merrion Way  
Leeds LS2 8PB West Yorkshire(GB)(54) **3-Aryl-5,6-dihydro-1,4,2-oxathiazines and their oxides.**

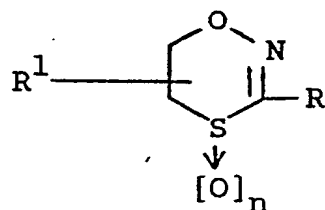
(57) Disclosed are derivatives of 3-aryl-5,6-dihydro-1,4,2-oxathiazines and their oxides for use as herbicides, fungicides, plant dessicants and defoliants in agricultural and biocidal applications. Also disclosed are methods of making these compounds.

**EP 0 104 940 A1**

This invention relates to derivatives of 3-aryl-5,6-dihydro-1,4,2-oxathiazines and their oxides, and to the use of such derivatives as herbicides, fungicides, and plant dessicants and defoliant. The invention also relates to methods of preparing these chemicals.

Dihydro 1,4,2-oxathiazines are little known in the chemical literature. A multi-substituted compound, N-(5,6-dihydro-5,6-dimethyl-3-phenyl-1,4,2-oxathiazine-6-yl)acetamide, was reported in Tetrahedron Letters, 1972, p. 5267, and a tetrahydro compound was described in J. Org. Chem. 30:949 (1965). However, no utility was disclosed for these compounds.

The chemicals of this invention are represented by the general formulae below, and possess herbicidal activity, fungicidal activity and plant desiccating and defoliating activities.



wherein n is 0, 1 or 2, R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl or benzyl, and R has one of the following values:

phenyl or naphthyl;

phenyl substituted with 1 or 2 of the following groups:

hydroxyl

halo

C<sub>1</sub>-C<sub>12</sub> alkyl

C<sub>5</sub>-C<sub>6</sub> cycloalkyl

trihalomethyl

- phenyl  
 $C_1-C_5$  alkoxy or alkylthio  
 tetrahydropyranyloxy  
 phenoxy  
 5  $C_2-C_5$  alkylcarbonyl  
 phenylcarbonyl  
 $C_1-C_4$  alkylsulfinyl  
 $C_1-C_4$  alkylsulfonyl  
 carboxy or its alkali metal salt  
 10  $C_2-C_5$  alkoxy carbonyl  
 $C_2-C_5$  alkylaminocarbonyl  
 phenylaminocarbonyl  
 tolylaminocarbonyl  
 morpholinocarbonyl  
 15 amino  
 nitro  
 cyano or  
 dioxolanyl;  
 pyridinyl;  
 20 thienyl provided n is not 2;  
 furanyl;  
 furanyl substituted with 1 to 3 of the following groups:  
 $C_1-C_4$  alkyl and  
 $C_2-C_5$  alkoxy carbonyl.  
 25 In preferred compounds of the foregoing formula,  $R^1$  is hydro-  
 gen or  $C_1-C_4$  linear or branched alkyl and R has one of the follow-  
 ing values:  
 phenyl;  
 phenyl substituted with 1-2 of the following groups:  
 30 F, Cl, Br, except not 2-Cl or 2,4- $Cl_2$  if n is 2  
 $C_1-C_4$ , except p-t-alkyl if n is zero  
 $CF_3$   
 phenyl except if n is 2  
 $C_1-C_5$  alkoxy  
 35  $C_2-C_5$  alkylcarbonyl  
 $C_2-C_5$  alkoxy carbonyl except 4-alkoxy carbonyl if n is zero

amino  
nitro or  
cyano;

3- or 4-pyridinyl provided n is not 2

5 thienyl provided n is not 2;

furanyl;

furanyl substituted with 1 to 3 of the following groups:

methyl or

C<sub>2</sub>-C<sub>3</sub> alkoxycarbonyl.

10 In more preferred compounds of the above formula, R<sup>1</sup> is hydrogen or methyl and R has one of the following values:

phenyl provided n is not 2;

phenyl substituted with 1 or 2 of the following groups:

F, Cl, Br, but not 2-Cl or 2,4-Cl<sub>2</sub> if n is 2

15 n-C<sub>1</sub>-C<sub>4</sub> alkyl

CF<sub>3</sub>

C<sub>1</sub>-C<sub>2</sub> alkoxy

C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl, provided n is 1

C<sub>2</sub>-C<sub>3</sub> alkoxycarbonyl provided n is 1 or 2

20 nitro or

cyano;

3- or 4-pyridinyl provided n is 0 or 1;

thienyl provided n is 0 or 1;

furanyl;

25 furanyl substituted with 1 to 3 methyl groups, provided n is 1 or 2.

Compounds of the invention may be used for control of various grasses and broadleaved weeds including pigweed (Amaranthus retroflexus L.), velvetleaf (Abutilon theophrasti Medic.), jimson-  
30 weed (Datura stramonium L.), tall morning-glory (Ipomoea purpurea (L.) Roth), barnyardgrass (Echinochloa crusgalli (L.) Beauv.), green foxtail (Setaria viridis (L.) Beauv.) giant foxtail (Setaria faberi Herrm.), crabgrass (Digitaria ischaemum (Schreb.) Muhl.) and switchgrass (Panicum virgatum L.).

35 Chemical harvest aids are used for a wide variety of primary effects, including the defoliation of the crop plant; the desiccation of its leaves, stems, and other aerial organs; the control of late-

season regrowth (e.g. cotton); the concentration of crop maturity providing more efficient harvesting.

Under normal conditions, many crop plants do not mature uniformly or in a timely fashion, so that efficient, optimum harvest is difficult, either due to equipment scheduling or to weather. Crops such as cotton, potato, sunflower, seed legumes and other oilseed crops require either desiccation or defoliation before harvest can be effectively accomplished. Cotton is an example of a crop with a long history of successful harvest aid use. When cotton is adequately defoliated, mechanical pickers can operate more effectively. If the crop is not defoliated, the leaves can interfere with the picking mechanism. Also, leaves can contaminate the cotton lint with trash or green stain, which reduces the quality of the fiber or reduces the efficiency of the ginning process. Likewise, potato vines need to be desiccated for efficient mechanical digging. In addition, upon desiccation of potato leaves and haulms, the tuber skin matures and becomes less susceptible to damage from the digger and post-harvest handling. Seed legumes and sunflowers are also mechanically harvested, and this process is facilitated if the leaves are removed or desiccated. As with cotton and potato, such defoliation or desiccation also ripens the seed uniformly, accelerates the rate of fruit maturation, and conditions the pod or head for easy harvest.

Compounds of this invention have been found to have surprising utility as harvest aid chemicals. Specifically, when applied to the foliage of crop species, they cause desiccation and/or defoliation of the leaves, can cause desirable changes in the fruiting form (e.g. cotton boll), and may alter the re-growth of the plant.

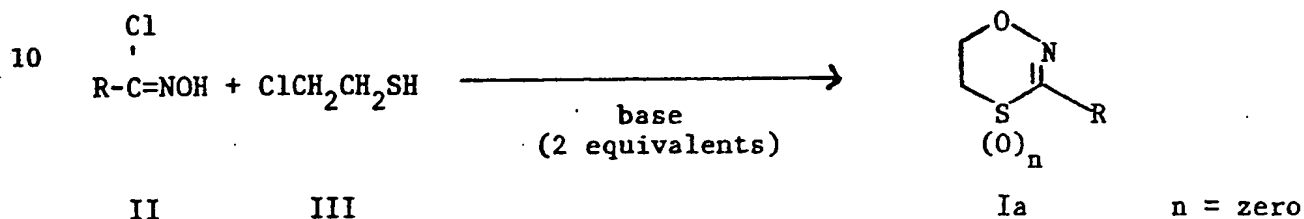
Applications of the compounds may be in the form of aqueous solutions or suspensions applied to the target tissue. Compounds of this invention may be used alone, in combination with one or more other oxathiazine derivative described here, or as a tank mix with other harvest aid chemical compounds or spray adjuvants (such as surface-active agents, stickers, emulsifiers, or extenders).

In addition, the chemicals described for this invention possess antifungal properties which are useful for the control of plant diseases such as Rice Blast, Bean Rust, Tomato Early Blight,

Cercospora Leaf Spot or similar diseases. Growth inhibition tests indicate a broad spectrum of activity against other disease-producing fungi such as Alternaria, Sclerotium, Piricularia, Pythium, Phytophthora, Fusarium.

- 5 Two methods of synthesizing the chemicals of this invention have been discovered. One of these is outlined in Scheme I below and utilizes aromatic aldehydes as starting materials.

SCHEME I



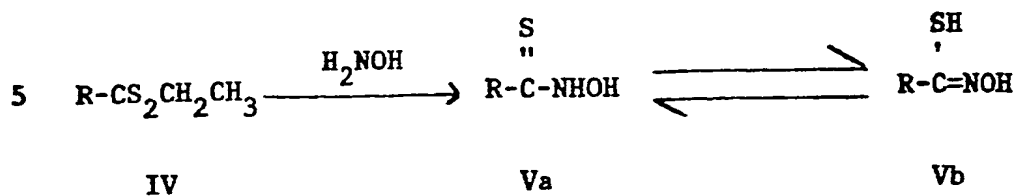
- 15 N-hydroxyarylcarboximidoyl chloride (II) is treated with 2-chloroethanethiol in the presence of two equivalents of base or suitable hydrogen chloride scavenger to produce 3-aryl-5,6-dihydro-1,4,2-oxathiazine (I, n = 0). The II intermediate may be readily made by known methods by converting an aldehyde of the
- 20 formula RCHO to its corresponding oxime (RCH = NOH) in the presence of H<sub>2</sub>NOH and subsequent chlorination with chlorine or t-butyl hypochlorite in methylene chloride or chloroform as the solvent. If only one equivalent of base is used, the intermediate 2-chloroethyl N-hydroxybenzene-carboximidothioate derivative is
- 25 isolated. This intermediate will give the oxathiazine when treated with a base.

Oxidation of oxathiazines with peroxyacetic acid or m-chloro-peroxybenzoic gives the oxides (I, n = 1 or 2).

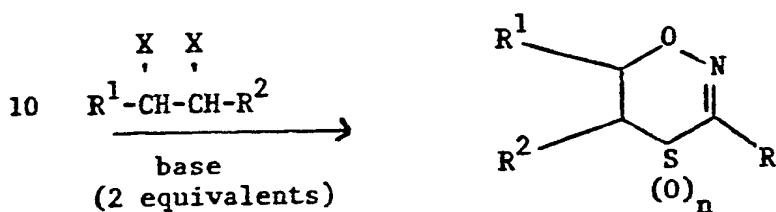
- 30 Scheme II below outlines the second method of preparation, which uses arylcarbodithioate esters.

## SCHEME II

## Step I



## Step 2



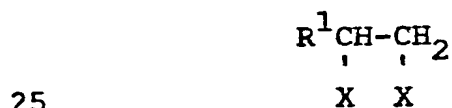
Ib

X = halogen (Cl, Br, I)

n = zero

15  $\text{R}^1$  and  $\text{R}^2$  = hydrogen,  $\text{C}_1$ - $\text{C}_4$  alkyl or benzyl  
provided at least one of  $\text{R}^1$  and  $\text{R}^2$   
is hydrogen

Treatment of a carbodithioate ester (IV) with hydroxylamine results in the liberation of ethyl mercaptan and the formation of N-hydroxyarylthioamide (Va) which enolises to N-hydroxyarylcarboximidothioic acid (Vb). Formation of the oxathiazine is then accomplished by reacting with vicinal dihaloalkane,



( $\text{R}^1$  and X as previously described) in the presence of two equivalents of base. A minor impurity is sometimes obtained in this reaction. For example, when two molecules of N-hydroxycarboximidothioic acid (Vb) react with one molecule of 1,2-dibromoethane, 1,2,-ethanediyl bis(N-hydroxyarylcarboximidothioate) is produced and can be extracted from the reaction by washing with dilute aqueous sodium hydroxide.

In Scheme I, the reaction of compound II with compound III for the preparation of the desired oxathiazine of this invention may be carried out at a temperature of minus 10 to plus 20°C. Usually, the reaction takes about 0.5-6 hours for completion but ordinarily  
5 does not take longer than 3 hours.

In Scheme II, the Step I reaction is performed at from 0 to 30°C, usually at 10-25°C, and it may take 0.5-2 hours, generally 0.5-1 hour to form the Va/Vb equilibrium product. In Step 2, a  
10 temperature of 0-100°C may be employed although a 20-80°C temperature range is more preferred. The reaction usually takes from 0.5 to 5 hours, but in many cases completion can be obtained within 3 hours. As solvents, C<sub>1</sub>-C<sub>10</sub> aliphatic alcohols may be used or aprotic solvents such as dimethylformamide or dimethylsulfoxide.

If so desired, intermediate compounds suitable for making the  
15 chemicals of this invention may be prepared having the structural formula  $RC(=NOH)SCH_2CH_2Cl$  by using Scheme I of this invention wherein R has the meanings of claim 1, R<sup>1</sup> is hydrogen and n is 0, using only one equivalent of base such as alkali metal C<sub>1</sub>-C<sub>10</sub> alkoxide, alkylamines, alkanolamines, pyridine, morpholine and  
20 similar organic bases.

The preparation of the compounds can best be illustrated by the following specific examples.

Compound numbers are in parenthesis (c.f. Tables 1 to 4).

#### Example 1

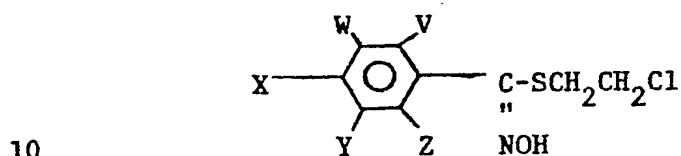
##### 25 2-Chloroethyl 2-chloro-N-hydroxybenzenecarboximidothioate

2-Chlorobenzaldoxime (46.7 g, 0.3 mol) in chloroform (350 ml) was cooled and stirred in an ice/salt bath. Chlorine gas was bubbled into the reaction until an excess was present. Excess chlorine and solvent were removed and the remaining 2-chloro-N-  
30 hydroxybenzenecarboximidoyl chloride dissolved in ether (250 ml). Solutions of triethylamine (30.3 g, 0.3 mol) in ether (50 ml) and 2-chloroethanethiol (29 g, 0.3 mol) in ether (50 ml) were added simultaneously with stirring and cooling. After the addition, the reaction was allowed to warm to room temperature and left over-  
35 night. Water was added, and the ether layer was washed with additional water, then dried with anhydrous magnesium sulphate.



Evaporation left a white solid, 2-chloroethyl 2-chloro-N-hydroxybenzenecarboximidothioate, m.p. 115-117°C., (Found: C, 43.29; H, 3.58; N, 5.59.  $C_9H_9Cl_2$  NOS requires C, 43.21; H, 3.62; N, 5.60).

- 5 The following compounds of this type were prepared in a similar manner.



	V	W	X	Y	Z	m.p. °C
	H	H	Cl	H	H	110-117
	Cl	H	Cl	H	H	104-106
	H	H	CH <sub>3</sub>	H	H	118-119
15	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	86-96

#### Example 2

##### 3-(2-Chlorophenyl)-5,6-dihydro-1,4,2-oxathiazine (3)

20 2-Chlorethyl 2-chloro-N-hydroxybenzenecarboximidothioate (25 g, 0.1 mol) was added to a cold solution of sodium (2.3 g) in ethanol (150 ml). An exotherm was observed. The reaction was left at room temperature overnight, then the ethanol was removed, the product extracted with ether, the ether solution washed with water, dried and evaporated to leave an oil. Distillation b.p. 121° C at 0.02 mm (2.67 pa) gave an oil which solidified, 3-(2-chloro-phenyl)-5,6-dihydro-1,4,2-oxathiazine, m.p. 51-52°C. (Found: C, 50.30; H, 3.73; N, 6.57.  $C_9H_8ClNOS$  requires C, 50.58; H, 3.77; N, 6.55).

#### Example 3

##### 5,6-Dihydro-3-(4-pyridinyl)-1,4,2-oxathiazine (11)

30 4-Pyridinecarboxaldehyde oxime (30.6 g, 0.25 mol) was chlorinated in chloroform (350 ml) as described in Example 1 to produce N-hydroxy-4-pyridine-carboximidoyl chloride which was suspended in ether (500 ml) containing 2-chloroethanethiol (26.9 g, 0.25 mol). With ice bath cooling, triethylamine (5.1 g, 0.5 mol) was added dropwise. After the addition, water was made, the suspended

35

solid, crude 2-chloroethyl N-hydroxy-4-pyridinecarboximidothioate was collected on a filter and dried. This crude ester was added to a solution of sodium ethoxide (from 5.75 g sodium in 500 ml ethanol), and the reaction mixture stirred for 4 hours. Water was added and the product was extracted with ether to give 5,6-dihydro-3-(4-pyridinyl)-1,4,2-oxathiazine, mp 80-82°C, (found: C, 53.16; H, 4.56; N, 15.07.  $C_8H_8N_2OS$  requires C, 53.33; H, 4.48; N, 15.55).

#### Example 4

##### 10 5,6-Dihydro-3-[3-trifluoromethyl]phenyl]-1,4,2-oxathiazine (45)

Ethyl 3-(trifluoromethyl)benzenecarbodithioate (24.7 g, 0.1 mol) was dissolved in ethanol (50 ml) in which was suspended hydroxylamine hydrochloride (7 g, 0.1 mol). With stirring, triethylamine (10.1 g, 0.1 mol) in ethanol (25 ml) was added dropwise. After 5 hours, ethyl mercaptan was removed under reduced pressure through a KOH scrubber. 1,2-Dibromoethane (19 g, 0.1 mol) was added to the reaction mixture followed by dropwise addition of triethylamine (30 ml) in ethanol (50 ml). A white precipitate formed. After the addition was complete, the reaction mixture was warmed until it was homogeneous, then left at room temperature overnight. Water was added, the product extracted into ether, the ether solution washed with dilute sodium hydroxide (2N approx.), then water, dried over anhydrous magnesium sulphate and evaporated to leave an oil which was distilled to give 5,6-dihydro-3-[3-(trifluoromethyl)phenyl]-1,4,2-oxathiazine, bp 113°/0.2 mm.

#### Example 5

##### 5,6-Dihydro-3-(2-furanyl)-1,4,2-oxathiazine (31)

Methyl 2-furancarboxidithioate (30 g, 0.2 mol) was converted to 5,6-dihydro-3-(2-furanyl)-1,4,2-oxathiazine, an oil, bp 128-129°C at 1.3 mm (173 Pa), (preparation similar to Example 4). The sodium hydroxide wash from the ether extract was acidified. An amber oil separated out and on standing, solidified. This solid was collected, washed with ether, dried and found to be 1,2-ethandiyldis(N-hydroxy-2-furancarboximidothioate), mp 147-150°C. (Found: C, 45.80; H, 4.08; N, 8.62.  $C_{12}H_{12}N_2O_4S_2$  requires C, 46.16; H, 3.87; N, 8.97.)

Example 65,6-Dihydro-3-(3-fluorophenyl)-1,4,2-oxathiazine, 4-oxide (28)

5,6-Dihydro-3-(3-fluorophenyl)-1,4,2-oxathiazine (19.7 g, 0.1 mol) was dissolved in chloroform, 50 ml). 3-Chloroperoxybenzoic acid (21 g) dissolved in chloroform (200 ml) was added dropwise at such a rate that the temperature of the reaction mixture remained at between 25° to 30°C. After the addition was complete, the reaction was left stirring at room temperature overnight. Saturated aqueous sodium bicarbonate was added and stirred until all gassing ceased. The chloroform solution was washed with water, dried over anhydrous magnesium sulphate and evaporated to leave a solid which was recrystallised from ether/ligroin, to give 5,6-dihydro-3-(3-fluorophenyl)-1,4,2-oxathiazine 4-oxide, mp 79°C.

Example 75,6-Dihydro-3-(3-chlorophenyl)-1,4,2-oxathiazine, 4-oxide (84)

5,6-Dihydro-3-(3-chlorophenyl)-1,4,2-oxathiazine (21.4 g, 0.1 mol) in methylene chloride (50 ml) was cooled with ice water. 3-Chloroperoxybenzoic acid (21 g, 85%) in methylenechloride (150 ml) was added dropwise the reaction was stirred and the temperature maintained at 10°C. After the addition, the reaction was brought to ambient temperature and stirred overnight. After washing with aqueous sodium bicarbonate, water and then drying over anhydrous magnesium sulphate, evaporation of the solvent left a solid which was washed with ether and dried to leave 5,6-dihydro-3-(3-chlorophenyl)-1,4,2-oxathiazine, 4-oxide, mp 112-4°C. (Found: C, 47.03; H, 3.43; N, 6.21.  $C_9H_8ClNO_2S$  requires C, 47.07, H, 3.51, N, 6.09.)

Example 83-(2,6-Dichlorophenyl)-5,6-dihydro-1,4,2-oxathiazine, 4,4-dioxide

(56)

3-(2,6-Dichlorophenyl)5,6-dihydro-1,4,2-oxathiazine was oxidised as in Example 6 except that two equivalents of 3-chloroperoxybenzoic acid were used. Thus, 3-(2,6-dichlorophenyl)-5,6-dihydro-1,4,2-oxathiazine 4,4-dioxide, mp 180-182°C was prepared. (Found: C, 38.40; H, 2.56; N, 5.02.  $C_9H_7Cl_2NO_3S$  requires C, 38.58; H, 2.51; N, 5.00.)

Example 9

3-(3-Chlorophenyl)-5,6-dihydro-1,4,2-oxathiazine (26)

Ethyl 3-chlorobenzenecarbodithioate (106 g, 0.5 mol) and ethanol (400 ml) was treated with finely powdered hydroxylamine hydrochloride (36 g, 0.5 mol, 97%) with stirring, triethylamine (50.5 g, 70 ml, 0.5 mol) was added dropwise. A slight exotherm was observed. After the addition, the reaction was stirred for 1½ hours. Ethyl mercaptan was removed using a scrubber and vacuum trap. 1,2-Dibromoethane (95 g, 0.5 mol) was added to the reaction and with stirring, triethylamine (101 g, 140 ml, 1 mol) added dropwise. The initial red colour was completely discharged. When the addition was complete, the reaction was refluxed for 1 hour, cooled to room temperature and the solvent removed to leave a solid. Water was added, the product extracted into ether which was subsequently washed successively with water, 5% potassium hydroxide, water and then dried over anhydrous magnesium sulphate. After evaporation, a white solid remained, 3-(3-chlorophenyl)-5,6-dihydro-1,4,2-oxathiazine, mp 65°C.

Example 10

3-(3-Fluorophenyl)-5,6-dihydro-1,4,2-oxathiazine (27)

2-Chloroethyl 3-fluoro-N-hydroxybenzenecarboximidodithioate was made in a manner similar to that described in Example 1 using the following materials:

- 3-Fluorobenzaldehyde oxime (27.8 g, 0.2 mol)
- 2-Chloroethanethiol (21.5 g, 0.2 mol)
- Triethylamine (40.8 g, 0.4 mol)
- Ether (400 ml)

Cyclisation of 2-chloroethyl 3-fluoro-N-hydroxybenzenecarboximidodithioate was accomplished as described in Example 2 using sodium (4.6 g) in ethanol (300 ml) to give 3-(3-fluorophenyl)-5,6-dihydro-1,4,2-oxathiazine, mp 47-9°C. (Found: C, 54.66; H, 4.13; N, 7.07.  $C_9H_8FNOS$  requires C, 54.81; H, 4.09; N, 7.10).

Example 115,6-Dihydro-3-(3-nitrophenyl)-1,4,2-oxathiazine (12)

5,6-Dihydro-3-(3-nitrophenyl)-1,4,2-oxathiazine, mp 114-5°C, was prepared in a manner as described in Example 9 using the following materials:

- Methyl 3-nitrobenzenecarbodithioate, (117 g, 0.55 mol)
- Ethanol (250 ml)
- Hydroxylamine hydrochloride (40 g, 0.55 mol)
- 1,2-Dibromoethane (40 ml)
- 10 Triethylamine (80 ml) and a further (160 ml).

Example 123-(4-Chlorophenyl)-5,6-dihydro-1,4,2-oxathiazine (1)

2-Chloroethyl 4-chloro-N-hydroxybenzenecarboximidothioate (2.5 g, 0.01 mol) was cyclised with sodium (0.23 g) in ethanol (25 ml) as described in Example 2. 3-(4-Chlorophenyl)-5,6-dihydro-1,4,2-oxathiazine, mp 80.5-81.5°C, was isolated. (Found: C, 50.16; H, 4.24; N, 6.44.  $C_9H_8ClNOS$  requires C, 50.58; H, 3.77; N, 6.55.)

Example 13(3-(4-Bromophenyl)-5,6-dihydro-1,4,2-oxathiazine (70)

20 3-(4-Bromophenyl)-5,6-dihydro-1,4,2-oxathiazine, mp 114-5°C, was made as described in Example 9 using the following materials:

- Ethyl 4-bromobenzenecarbodithioate (130.5 g, 0.5 mol)
- Ethanol (500 ml)
- Hydroxylamine hydrochloride (97%) (36 g, 0.5 mol)
- 25 1,2-dibromoethane (45 ml)
- Triethylamine (72 ml) and a further (140 ml).

Example 143-(3,5-dichlorophenyl)-5,6-dihydro-1,4,2-oxathiazine (64)

30 3-(3,5-Dichlorobenzenecarbodithioate (50 g, 0.2 mol), mp 88-9°C

- Ethanol 250 ml
- Hydroxylamine hydrochloride 14.5 g, 0.2 mol
- Triethylamine (28 ml) in ethanol (30 ml)

1,2-dibromoethane (25 ml)

Triethylamine (56 ml)

Example 15

5,6-Dihydro-3-(2-thienyl)-1,4,2-oxathiazine (37)

- 5        5,6-Dihydro-3-(2-thienyl)-1,4,2-oxathiazine, mp 86-89°C, was made as described in Example 9 using the following materials:
- Methyl 2-thiophenecarbodithioate (35 g, 0.2 mol)
- Ethanol (100 ml)
- Hydroxylamine hydrochloride (14 g, 0.2 mol)
- 10        1,2-Dibromoethane (37.6 g, 0.2 mol)
- Triethylamine (28 ml) and a further (56 ml)

Example 16

Ethyl 4-(5,6-dihydro-1,4,2-oxathiazine-3-yl)benzoate (80)

- Ethyl 4-(5,6-dihydro-1,4,2-oxathiazine-3-yl)benzoate, mp
- 15        69-70°C was prepared as outlined in Example 9 using the following:
- Ethyl 4-[(methylthio)thioxomethyl]benzoate (83 g, 0.35 mol)
- Ethanol (200 ml)
- Hydroxylamine hydrochloride (97%) (25 g, 0.35 mol)
- Triethylamine (50 ml) in ethanol (50 ml)
- 20        1,2-Dibromoethane (30 ml)
- Triethylamine (100 ml).

Example 17

3-(3-Chlorophenyl)-5,6-dihydro-5-(or 6)-methyl-1,4,2-oxathiazine (92)

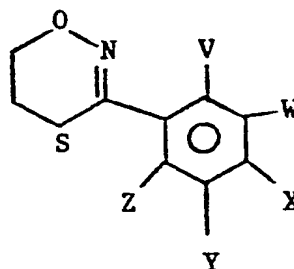
- 25        3-(3-Chlorophenyl)-5,6-dihydro-5-(or 6)-methyl-1,4,2-oxathiazine, bp 145°C at 0.25 mm (33.3 Pa), was prepared as described in Example 9 using the following:
- Ethyl 3-chlorobenzenecarbodithioate (43.2 g, 0.2 mol)
- Ethanol 200 (ml)
- 30        Hydroxylamine hydrochloride (14.5 g, 0.2 mol)
- 1,2-Dibromopropane (40.5 g, 0.2 mol)
- Triethylamine (28 ml) and a further (56 ml).

## Example 18

[(3-(5,6-Dihydro-1,4,2-oxathiazine-3-yl))-N-phenylbenzamide (100)

3-(5,6-Dihydro-1,4,2-oxathiazine-3-yl)benzoic acid (15 g, 0.07 mol) was suspended in methylene chloride (200 ml). Thionyl chloride (10 ml) was added and the reaction was refluxed until homogeneous and all gassing had ceased. The solvent was removed, the remaining oil was taken up in methylene chloride and treated portionwise with aniline (12.5 g, 0.12 mol). An exotherm was observed. After several hours, water was added, the organic material separated, washed successively with water, aqueous bicarbonate, dilute hydrochloric acid, water and then dried over anhydrous magnesium sulphate. Evaporation of the solvent left a solid which was recrystallised from ethanol to give crystals of 3-(5,6-dihydro-1,4,2-oxathiazin-3-yl)-N-phenylbenzamide, mp 149-150°C. (Found: C,64.65; H,4.92; N,9.65.  $C_{16}H_{14}N_2O_2S$  requires C,64.42; H,4.73; N,9.39).

TABLE 1



COM- 25	POUND	V	W	X	Y	Z	m.p.°C or bp.
	1	H	H	Cl	H	H	80.5-81.5
	3	Cl	H	H	H	H	51-52, 121 at 0.02mm (2.67 Pa)
	6	Cl	H	Cl	H	H	137-141° at 0.05 mm (6.67 Pa)
	8	H	H	CH <sub>3</sub>	H	H	125-128° at 1.5 mm (200 Pa)
30	9	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	139-140° at 0.4 mm (53.3 Pa)
	12	H	NO <sub>2</sub>	H	H	H	114-115
	13	H	Cl	Cl	H	H	77-78
	16	CH <sub>3</sub>	H	H	H	H	160 at 3 mm (400 Pa)
	18	H	H	H	H	H	47-49
35	26	H	Cl	H	H	H	65

TABLE 1 (cont'd.)

COM- POUND	V	W	X	Y	Z	m.p. °C or bp.
27	H	F	H	H	H	47-49
5 30	H	CH <sub>3</sub>	H	H	H	52-54
34	H	H	OCH <sub>3</sub>	H	H	91-92
35	H	OCH <sub>3</sub>	H	H	H	oil
39	H	H	F	H	H	46-48; 90° at 0.05 mm (6.67 Pa)
47	Cl	H	H	H	F	oil
10 48	H	H	CN	H	H	115-118
51	H	H	COCH <sub>3</sub>	H	H	128-129
54	Cl	H	H	H	Cl	96-97
60	H	H	OC <sub>6</sub> H <sub>5</sub>	H	H	98-100
62	H	H	COC <sub>6</sub> H <sub>5</sub>	H	H	125-126
15 63	H	H	O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H	H	96-7
64	H	Cl	H	Cl	H	88-9
69	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	H	H	86-90
70	H	H	Br	H	H	114-5
71	H	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H	H	Oil
20 78	H	H	CF <sub>3</sub>	H	H	110-1
80	H	H	CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	H	H	69-70
79	H	H	CO <sub>2</sub> H	H	H	225
87	H	CO <sub>2</sub> CH <sub>3</sub>	H	H	H	65-6
45	H	CF <sub>3</sub>	H	H	H	113° at 0.2 mm (26.7 Pa)
25 88	H	H	C <sub>6</sub> H <sub>5</sub>	H	H	147-150
89	H	Br	H	H	H	95-97
93	H	CO <sub>2</sub> H	H	H	H	168-171
98	H	H	SCH <sub>3</sub>	H	H	104-105
99	H	H	CONH-C <sub>6</sub> H <sub>4</sub> - 2-CH <sub>3</sub>	H	H	183-185
30 100	H	CONHC <sub>6</sub> H <sub>5</sub>	H	H	H	149-150
101	H	H	SOCH <sub>3</sub>	H	H	116-117
107	H	H	O-2-Tetra- hydropyranyl	H	H	93-94
35 108	H	H	OCH <sub>2</sub> CH <sub>3</sub>	H	H	95-96
109	H	H	OC <sub>5</sub> H <sub>11</sub>	H	H	93-95



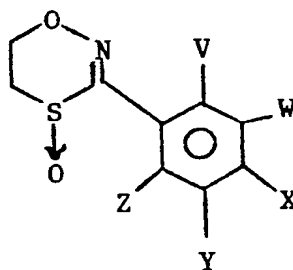
TABLE 1 (cont'd.)

COM- POUND	V	W	X	Y	Z	m.p.°C or bp.
92 <sup>(2)</sup>	H	Cl	H	H	H	145/0.25 mm
5 110	H	H	CO-4-Morph- oliny1	H	H	125-126
111	H	CH <sub>3</sub>	NO <sub>2</sub>	H	H	116-117
115	H	NH <sub>2</sub>	H	H	H	71-74
116	H	CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	H	H	H	47-49
10 117	H	H	CO <sub>2</sub> CH <sub>3</sub>	H	H	142-143
118	H	H	CO <sub>2</sub> K	H	H	>250
119	H	H	OH	H	H	160-161
125	H	COOK	H	H	H	>250
126 <sup>(1)</sup>	H	Cl	H	H	H	51-54.5
15 127	H	H	NO <sub>2</sub>	H	H	168-170
130	H	CN	H	H	H	70-72
132	F	H	H	H	H	125/0.25 mm
139 <sup>(2)</sup>	Cl	H	H	H	H	oil
140 <sup>(3)</sup>	H	Cl	H	H	H	oil

- 20 (1) Methyl group on 6- position of the 1,4,2-oxathiazine ring.  
 (2) Methyl group on 5- or 6- position of the 1,4,2-oxathiazine ring.  
 (3) Methyl group on 5- position of the 1,4,2-oxathiazine ring.

TABLE 2

25



30	COMPOUND	V	W	X	Y	Z	m.p.°C
	5	H	H	Cl	H	H	72-75
	15	H	NO <sub>2</sub>	H	H	H	149-153
	19	H	Cl	Cl	H	H	104-7
	28	H	F	H	H	H	78-81
35	29	H	H	H	H	H	68-70

TABLE 2 (cont'd.)

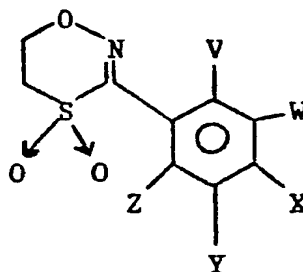
	COMPOUND	V	W	X	Y	Z	m.p. °C
	32	H	CH <sub>3</sub>	H	H	H	68-69
	36	H	H	OCH <sub>3</sub>	H	H	109-112
5	41	H	OCH <sub>3</sub>	H	H	H	62-64
	42	H	H	CH <sub>3</sub>	H	H	100-102
	46	H	CF <sub>3</sub>	H	H	H	89-90
	52	H	H	COCH <sub>3</sub>	H	H	159-160
	55	Cl	H	H	H	Cl	133-135
10	61	H	H	OC <sub>6</sub> H <sub>5</sub>	H	H	155-157
	67	H	H	O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H	H	77-8
	68	H	Cl	H	Cl	H	135-6
	73	H	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H	H	68
	75	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	H	H	101-3
15	76	H	H	Br	H	H	113-5
	82	H	H	CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	H	H	106-8
	84	H	Cl	H	H	H	112-4
	86	H	H	CF <sub>3</sub>	H	H	142-5
	91	H	CO <sub>2</sub> CH <sub>3</sub>	H	H	H	103-104
20	95	H	H	C <sub>6</sub> H <sub>5</sub>	H	H	138-144
	96	H	Br	H	H	H	104-106
	102	H	CONHC <sub>6</sub> H <sub>5</sub>	H	H	H	158-160
	103	H	H	SOCH <sub>3</sub>	H	H	140-142
	104	H	H	SO <sub>2</sub> CH <sub>3</sub>	H	H	160-163
25	112	H	H	CONHC <sub>6</sub> H <sub>4</sub> - 2-CH <sub>3</sub>	H	H	168-169
	113	H	H	OC <sub>5</sub> H <sub>11</sub>	H	H	68-70
	120	H	CH <sub>3</sub>	NO <sub>2</sub>	H	H	156-158
	121	H	H	CO-morph- olinyll	H	H	182-183
30	122	H	H	OCH <sub>2</sub> CH <sub>3</sub>	H	H	125-127
	133	H	CN	H	H	H	153-155
	134	H	H	COOCH <sub>3</sub>	H	H	137-138

TABLE 2 (cont'd.)

	COMPOUND	V	W	X	Y	Z	m.p. °C
	135 <sup>(1)</sup>	H	Cl	H	H	H	95-99.5
	136	H	H	NO <sub>2</sub>	H	H	190-193
5	140	Cl	H	H	H	H	94-95
	141	F	H	H	H	H	102-104

(1) Methyl group on 6- position of the 1,4,2-oxathiazine ring.

TABLE 3



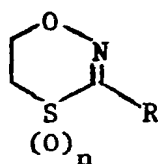
	COMPOUND	V	W	X	Y	Z	m.p. °C
15	4	Cl	H	H	H	H	125-127
	7	Cl	H	Cl	H	H	101.5-102
	17	H	NO <sub>2</sub>	H	H	H	135-140
	20	CH <sub>3</sub>	H	H	H	H	118-120
20	25	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	85-86
	43	H	H	CH <sub>3</sub>	H	H	131.5-132.5
	49	H	H	CN	H	H	115-118
	53	H	H	COCH <sub>3</sub>	H	H	142-144
	56	Cl	H	H	H	Cl	180-182
25	57	H	H	H	H	H	98-99
	58	H	Cl	Cl	H	H	145-147
	59	H	H	Cl	H	H	89-90
	65	H	Cl	H	Cl	H	133-4
	66	H	H	O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H	H	104-5
30	72	H	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H	H	88-90
	74	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	H	H	133-4
	77	H	H	Br	H	H	147-8

TABLE 3 (cont'd.)

	COMPOUND	V	W	X	Y	Z	m.p. °C
	81	H	H	CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	H	H	118-20
	83	H	Cl	H	H	H	102-4
5	85	H	H	CF <sub>3</sub>	H	H	158-9
	90	H	CO <sub>2</sub> CH <sub>3</sub>	H	H	H	101-102
	94	H	H	C <sub>6</sub> H <sub>5</sub>	H	H	142-145
	97	H	Br	H	H	H	99-102
	105	H	H	CONHC <sub>6</sub> H <sub>4</sub> - 2-CH <sub>3</sub>	H	H	212-213
10	106	H	CONHC <sub>6</sub> H <sub>5</sub>	H	H	H	162-163
	114	H	H	OC <sub>5</sub> H <sub>11</sub>	H	H	66-67
	123	H	H	CO-morpho- linyl	H	H	165-168
15	124	H	H	OCH <sub>2</sub> CH <sub>2</sub>	H	H	123-124
	128	H	CH <sub>3</sub>	NO <sub>2</sub>	H	H	140-141
	129	H	CF <sub>3</sub>	H	H	H	104-104.5
	137	H	H	COOCH <sub>3</sub>	H	H	173-176
	138 <sup>(1)</sup>	H	Cl	H	H	H	123-126
20	142	H	CN	H	H	H	155-159
	143	F	H	H	H	H	130-132

(1) Methyl group on 6- position of the 1,4,2-oxathiazine ring.

TABLE 4



5

COMPOUND	R	n	m.p. °C/bp.
14	2-pyridinyl	0	135-137
23	2-pyridinyl	1	180
10	3-pyridinyl	0	125-128 at 0.05 mm (6.67 Pa)
24	3-pyridinyl	1	46-51
21	4-pyridinyl	1	150-158
22	4-pyridinyl	2	185
33	2-furanyl	1	77-78
44	2-furanyl	2	92-93
15	37	0	86-89
38	2-thienyl	1	107-109
40	2,4,5-trimethyl-3-furanyl	0	mp 35; bp 132/0.1 mm (13.3 Pa)
11	4-pyridinyl	0	80-82
31	2-furanyl	0	128-129/1.3 mm
20	131	0	66-7
	4-ethoxycarbonyl-3,5-dimethyl-2-furanyl		

All of the above compounds in Tables 1 to 4 were confirmed by elemental analysis and/or N.M.R. spectra and/or infrared spectra.

Compounds within the contemplation of this invention include the following (n being 0, 1 or 2):

V	W	X	Y	Z	n
H	H	CONHC <sub>4</sub> H <sub>9</sub>	H	H	0 or 1
H	H	CONHCH <sub>3</sub>	H	H	0 or 1
H	H	CN	H	H	1
30	H	Cl	H	H	1
H	Cl	H	H	H	1 <sup>1</sup>

(1) Methyl group on 5- position of the 1,4,2-oxathiazine ring.

As indicated above, compounds of the invention are particularly useful in herbicidal, fungicidal, defoliant and desiccant appli-

cations, particularly in the form of an agricultural chemical formulation comprising an effective amount of the compound in admixture with a carrier therefor.

For herbicidal (post-emergent or pre-emergent) applications, a preferred class of compounds are those of the general formula given above, in which  $R^1$  is hydrogen,  $C_1-C_4$  linear or branched alkyl or benzyl,  $n$  is 0, 1 or 2 and  $R$  has one of the following values:

phenyl or naphthyl;

phenyl substituted with 1 or 2 of the following groups:

10 halogen except 2-Cl if  $n$  is 2

$C_1-C_{12}$  alkyl

$C_5-C_6$  cycloalkyl

trihalomethyl

$C_1-C_8$  alkoxy (but not  $C_4-C_8$  alkoxy if  $n$  is zero or 2)

15 phenoxy

tetrahydropyranyloxy

$C_1-C_8$  alkylthio

$C_1-C_4$  alkylsulfinyl

$C_1-C_4$  alkylsulfonyl

20  $C_2-C_5$  alkylcarbonyl provided  $n$  is 0 or 1

carboxyl or its alkali metal salt

2- or 3- $(C_2-C_5$  alkoxycarbonyl)

4- $(C_2-C_5$  alkoxycarbonyl) provided  $n$  is 0 or 1

$C_2-C_5$  alkylaminocarbonyl

25 morpholinocarbonyl

amino

nitro

cyano

dioxolanyl;

30 4-pyridinyl if  $n$  is zero or 1;

thienyl provided  $n$  is not 2;

furanyl;

furanyl substituted with 1 to 3 of the following groups:

$C_1-C_4$  alkyl

35  $C_2-C_5$  alkoxycarbonyl.

More preferred herbicidal compounds are those wherein:

$R^1$  is hydrogen or  $C_1-C_4$  linear or branched alkyl and  
if n is zero, 1 or 2,

R = phenyl substituted with 1 or 2 of the following groups:

- 3- $CF_3$
- 5         $n-C_1-C_4$  alkyl provided they are in 3- or 4-position;
- 3-pyridinyl;
- furanyl;
- furanyl substituted with 1 to 3 of the following groups:
- methyl
- 10         $C_2-C_3$  alkoxy carbonyl.

if n is zero or 1,

R = phenyl;

phenyl substituted with 1 or 2 of the following groups:

- F or Cl
- 15        trifluoromethyl;
- thienyl;

if n is 1,

R = phenyl substituted with 1 or 2 of the following groups:

- 4-Br
- 20        4- $CF_3$
- $C_1-C_5$  alkoxy
- 3-nitro
- 3-cyano.

Still more preferred herbicidal compounds are those wherein:

25         $R^1$  is hydrogen or methyl, and

if n is zero, 1 or 2,

R = phenyl substituted with 1 or 2 of the following groups:

- 4-Cl
- 3- or 4-( $n-C_1-C_3$  alkyl);

30        if n is 1 or 2,

R = 2-furanyl;

if n is 1,

R = phenyl;

phenyl substituted with 1 or 2 of the following groups:

- 35        3-Cl or 3-F
- 4-trifluoromethyl

3-methoxy  
3-nitro  
4-(C<sub>1</sub>-C<sub>4</sub> alkyl);  
2-thienyl;

5 if n is zero or 1,

R = 3-pyridinyl;

if n is zero,

R = phenyl substituted with one of the following groups:

10 2,4-Cl<sub>2</sub>  
2-Cl  
3-Cl  
4-F  
2-Cl-6-F.

15 For fungicidal applications, a preferred class of compounds are those of the formula given above, in which R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl or benzyl, n is 0, 1 or 2, and R has one of the following values:

phenyl or naphthyl;

phenyl substituted with 1-2 of the following groups:

20 hydroxyl  
halo  
C<sub>1</sub>-C<sub>12</sub> alkyl  
C<sub>5</sub>-C<sub>6</sub> cycloalkyl  
trihalomethyl  
25 phenyl  
C<sub>1</sub>-C<sub>5</sub> alkoxy or alkylthio  
C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl  
phenylcarbonyl  
C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl  
30 C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl  
carboxy or its alkali metal salt  
C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl  
C<sub>2</sub>-C<sub>5</sub> alkylaminocarbonyl  
phenylaminocarbonyl  
35 tolylaminocarbonyl  
morpholinocarbonyl, except when n is zero



amino  
nitro  
cyano  
dioxolanyl;

5 pyridinyl, except 4-pyridinyl if n is zero;  
thienyl provided n is not 2;  
furanyl;  
furanyl substituted with 1 to 3 of the following groups:

10  $C_1-C_4$  alkyl  
 $C_2-C_5$  alkoxycarbonyl.

More preferred fungicidal compounds are those wherein:  
 $R^1$  is hydrogen or  $C_1-C_4$  linear or branched alkyl, and  
if n is zero, 1 or 2,

15 R = phenyl or naphthyl;  
phenyl substituted with 1 or 2 of the following groups:  
F, Cl or Br in 3- or 4- positions;

if n is 1 or 2,

20 R = phenyl substituted with 1 or 2 of the following groups:  
3- or 4- ( $C_1-C_4$  alkyl)  
3- or 4- trifluoromethyl  
 $C_1-C_4$  alkoxy  
phenoxy  
 $C_2-C_5$  alkylcarbonyl  
 $C_2-C_3$  alkoxycarbonyl  
25 nitro  
cyano;

if n is 1,

30 R = biphenyl;  
3-cyanophenyl;  
4-pyridinyl;  
thienyl.

Still more preferred fungicidal compounds are those in which,  
 $R^1$  is hydrogen or methyl;  
n is 1 or 2;

35 R is phenyl;  
phenyl substituted with 1-2 of the following groups:

F or Cl  
 methyl  
 3-trifluoromethyl  
 3-methoxy  
 5 methylcarbonyl  
 3-methoxycarbonyl  
 4-methoxycarbonyl provided n is 1  
 4-ethoxycarbonyl  
 nitro;  
 10 2-thienyl if n is 1;  
 2-furanyl.

For desiccating plants, a preferred class of compounds are those in which R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl or benzyl and

15 if n is zero, 1 or 2,  
 R = phenyl or naphthyl;  
 phenyl substituted with 1-2 of the following groups:  
 Cl or Br in the 3-position  
 C<sub>1</sub>-C<sub>12</sub> alkyl in the 3- or 4 position  
 20 3-trihalomethyl  
 C<sub>1</sub>-C<sub>3</sub> alkoxy or alkylthio  
 C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl  
 C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl  
 carboxy or its alkali metal salt  
 25 3-methoxycarbonyl  
 4-ethoxycarbonyl  
 amino  
 cyano  
 dioxolanyl;  
 30 3-pyridinyl;  
 4-nitrotolyl;  
 furanyl;  
 furanyl substituted with 1-3 of the following groups:  
 C<sub>1</sub>-C<sub>4</sub> alkyl  
 35 C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl;  
if n is 1 or 2,

R = phenyl substituted with:

2-F or 4-Br

4-trihalophenyl

3-ethoxycarbonyl

5 4-methoxycarbonyl

4-nitro;

if n is zero or 1,

R = phenyl substituted with

2-Cl

10 2-methyl

2,5-(CH<sub>3</sub>)<sub>2</sub>

C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl

morpholinocarbonyl;

4-pyridinyl;

15 thienyl;

if n is zero,

R = phenyl substituted with

3-F

2,6-Cl<sub>2</sub> or 2-Cl-6-F;

20 R = 2-pyridinyl.

More preferred compounds for desiccating plants are those in which R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl and

if n is zero, 1 or 2,

R = phenyl;

25 phenyl substituted with

3-(Cl or Br)

3,4-Cl<sub>2</sub>

3-methoxy

3-CF<sub>3</sub>;

30 3-pyridinyl;

furanyl;

if n is zero or 1,

R = phenyl substituted with:

2-(Cl or F)

35 3- or 4-(n-C<sub>1</sub>-C<sub>4</sub> alkyl)

2,5-(CH<sub>3</sub>)<sub>2</sub>

3-trifluoromethyl  
3-methoxycarbonyl;  
4-pyridinyl;  
thienyl;

5     if n is zero,  
      R = phenyl substituted with  
          2-methyl;  
      if n is 1 or 2,  
      R = phenyl substituted with  
10       4-CF<sub>3</sub>;  
      if n is 1,  
      R = 3-nitrophenyl.

For defoliating plants a preferred class of compounds are those  
in which R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl or benzyl  
15 and

if n is zero, 1 or 2,  
      R = phenyl;  
          phenyl substituted with 1-2 groups:  
              3- or 4-halo  
20            3,5-Cl<sub>2</sub>  
              2-(C<sub>1</sub>-C<sub>4</sub> alkyl)  
              4-(C<sub>3</sub>-C<sub>4</sub> alkyl)  
              2,5-(CH<sub>3</sub>)  
              phenyl  
25            3-methoxy  
              4-(C<sub>2</sub>-C<sub>4</sub> alkoxy)  
              C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl  
              3- or 4-carboxy, alkali metal salt  
              4-methoxycarbonyl  
30            C<sub>2</sub>-C<sub>5</sub> alkylaminocarbonyl  
              phenylaminocarbonyl  
              amino  
              3-nitro  
              3-cyano;  
35            3- or 4-pyridinyl;  
              furanyl;  
      n is zero or 1,

R = phenyl substituted with:

2-halo  
2,4-dihalo  
2,5-(CH<sub>3</sub>)<sub>2</sub>  
4-CF<sub>3</sub>  
4-pentyloxy  
3-(C<sub>2</sub>-C<sub>3</sub> alkoxy carbonyl)  
morpholinocarbonyl;  
thienyl;

10 n is 1 or 2,

R = phenyl substituted with:

3-CF<sub>3</sub>  
4-methoxy  
4-nitro  
4-nitrotolyl  
3,4-Cl<sub>2</sub>;

n is zero,

R = phenyl

phenyl substituted with:

20

2-halo  
3-methyl  
3,5-(CH<sub>3</sub>)<sub>2</sub>  
phenoxy;

furanyl substituted with methyl and ethoxycarbonyl;

25

n is 1,

R = phenyl substituted with:

2,6-Cl<sub>2</sub>  
4-CH<sub>3</sub>  
4-ethoxycarbonyl;

30

n is zero or 2,

phenyl substituted with tolylaminocarbonyl or 2-methyl.

More preferred compounds for defoliating plants are those in which R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl and

if n is zero, 1 or 2,

35

R = phenyl substituted with:

3-halo  
3,5-Cl<sub>2</sub>  
3-methoxy

4-carboxy alkali metal salt

3-amino

• 3-nitro

3-cyano;

5 3- or 4-pyridinyl;

if n is zero or 1,

R = phenyl substituted with:

2-halo

4-(Br or Cl

10 2,4-Cl<sub>2</sub>

2,5-(CH<sub>3</sub>)<sub>2</sub>;

2-thienyl;

if n is zero, 1 or 2,

R = phenyl substituted with:

15 3-CF<sub>3</sub>

3-CH<sub>3</sub>-4-NO<sub>2</sub>

4-nitro

4-methoxy;

if n is 0,

20 R = phenyl substituted with:

phenoxy;

if n is 1,

R = phenyl substituted with

4-(C<sub>1</sub>-C<sub>4</sub> n-alkyl)

25 C<sub>2</sub>-C<sub>4</sub> alkoxy

4-methylcarbonyl

3-(C<sub>2</sub>-C<sub>3</sub> alkoxy carbonyl)

4-methoxycarbonyl.

30 For herbicidal applications, compounds of this invention may be added as a "tank mix" to other herbicide solutions so that the number of different weed species controlled in a single application will be increased.

35 The procedures for using the present oxathiazine derivatives as herbicides may be in accordance with conventional agricultural practice. The chemicals are ordinarily applied as formulations containing a carrier and/or surface-active agent. The formulation may contain more than one of the described oxathiazine derivatives if desired; other active herbicides may be included in the formula-

tion as well.

Thus, the chemical may be impregnated on finely divided or granular inorganic or organic carriers such as attapulgite clay, sand, vermiculite, ground corn cobs, activated carbon or other granular carriers known to the art. The impregnated granules may then be spread on the soil as preemergence herbicides. Furthermore, the chemical may be formulated as wettable powders by grinding them into a fine powder and mixing them with an inactive powdered carrier to which a surface active dispersing agent has been added. Typical powdered solid carriers are the various mineral silicates, e.g., mica, talc, pyrophyllite and clays. The wettable powder may then be dispersed in water and sprayed on the soil surface or weeds. Similarly, soluble or emulsifiable concentrate may be prepared by first dissolving the chemical in a solvent. The choice of solvent depends on the solubility of the particular chemical. Commonly used solvents are acetone, methyl ethyl ketone, C<sub>1</sub>-C<sub>8</sub> alcohols such as methanol, ethanol, butanol, hexanol and 2-ethylhexanol; toluene, xylene, chloroform, furfuryl alcohol, phenol, naphtha, petroleum ether, kerosene or other aliphatic cycloaliphatic or aromatic solvents. Usually, a surface active agent or dispersant is added to the solvent. The resultant concentrate is then dispersed in water and applied by spraying. Suitable surface active agents and dispersants are well known to those skilled in the art and reference may be had to McCutcheon's Detergents and Emulsifiers, 1980, Allured Publishing Corp., Ridgewood, New Jersey; or Hoffman et al. U.S. patents 2,614,916, cols, 2 to 4 and 2,547,724, cols, 3 and 4, for example of appropriate surface active agents. The concentration of active chemical in the formulation may vary widely, e.g., from 1 to 95%. For use as a preemergence herbicide, the chemical is applied to soil which contains weed and crop seed (either to the surface of the soil or incorporated into the upper 2.5 to 7.6 cm of soil).

The most suitable rate of application in any given case will depend on such factors as soil type, soil pH, soil organic matter content, the quantity and intensity of rainfall before and after treatment, the air and soil temperature, light intensity and light duration per day. All of these factors have an influence on the efficacy of the chemicals for use as herbicides.

### Example 18

To illustrate herbicide efficacy of the described 3-aryl-5,6-dihydro-1,4,2-oxathiazines, 600 mg chemical was dissolved in 10 ml organic solvent to which 30 mg conventional emulsifying agent (e.g., ethoxylated sorbitan monolaurate "Tween 20" [trademark]) was added; in most cases acetone was used as the solvent. The solution was diluted to 100 ml with distilled water. Twenty milliliters of this 6000 ppm solution was diluted to 250 ppm with distilled water. The chemical was applied at the rate of 11.2 kg/ha (kilograms per hectare) by drenching 46 ml of the 250 ppm solution on the surface of soil in 11.4 cm diameter plastic pots which had been sown with the following weed seeds: velvetleaf (Abutilon theophrasti Medic.) or rough pigweed (Amaranthus retroflexus L.), jimsonweed (Datura stramonium L.), tall morningglory (Ipomea purpurea (L.) Roth), crabgrass (Digitaria ischaemum (Schreb.) Muhl) or switchgrass (Panicum virgatum L.), barnyardgrass (Echinochloa crusgalli (L.) Beauv.) and giant foxtail (Setaria faberi Herrm.) or green foxtail (Setaria viridis (L.) Beauv.). The percent control of the weeds compared to untreated checks was determined two weeks after treatment. TABLE 5 shows the results with the preemergence herbicides of the invention prepared in accordance with the above examples.

### Example 19

To illustrate effectiveness of the described oxathiazines as postemergence herbicides, the 6000 ppm solutions described under Example 18 were atomized with a number 152 DeVilbiss (trademark) sprayer, wetting the foliage to the drip point. The weeds, which are the same species as described under Example 18, were treated six days after emergence. The percent control was evaluated two weeks after treatment. TABLE 6 shows the results with postemergence herbicides of the invention.



TABLE 5

## PREEMERGENCE HERBICIDE ACTIVITIES OF OXATHIAZINES AT 11.2 kg/ha

		PERCENT WEED CONTROL					
5		PIGWEEED OR VELVETLEAF*	JIMSON WEED	MORNING GLORY	BARNYARD GRASS	CRABGRASS OR SWITCH- GRASS**	GIANT OR GREEN*** FOXTAIL
	COMPOUND						
	5	98	0	0	10	0	25
	9	90	0	0	25	0	0
	10	90	75	0	50	25	0
	13	100	0	10	15	0	0
	18	100	0	0	0	0	0
10	27	85	0	0	0	0	0
	28	100	0	35	30	95	98***
	29	100	0	0	30	95	95***
	30	100	0	0	20	80	80***
	32	100	0	0	50	25	0***
15	33	95	98	0	50	0	25***
	36	100	0	0	15	0	0***
	37	100	0	0	0	0	0***
	38	100	0	0	35	30	30***
	39	100	0	100	0	0	0***
20	41	100	0	0	0	75	0***
	42	100	0	0	50	75	75***
	43	40	0	0	0	0	0***
	44	70	0	0	30	80	65***
	46	100	0	0	0	0	0***
25	47	-	95	0	0	100	100***
	54	-	0	0	80	90**	100***
	55	-	100	0	90	95**	75***
	56	-	100	0	50	80**	25***
	67	0*	0	0	40	20**	80***
30	68	0*	0	0	25	50**	95***
	73	0*	0	0	50	95**	50***
	75	0*	0	0	60	95**	95***
	76	0*	0	0	50	90**	95***
	78	0*	0	0	0	30**	50***

TABLE 5  
(cont'd)PREEMERGENCE HERBICIDE ACTIVITIES OF OXATHIAZINES AT 11.2 kg/ha

5	PERCENT WEED CONTROL						
	COMPOUND	PIGWEE OR VELVETLEAF*	JIMSON WEED	MORNING GLORY	BARNYARD GRASS	CRABGRASS OR SWITCH- GRASS**	GIANT OR GREEN*** FOXTAIL
10	84	0*	70	0	30	50**	0***
	86	0*	75	0	75	95**	95***
	122	0*	0	0	50	15**	60***
	129	100*	0	0	0	0**	90***
	133	0	0	0	50	30**	50***
	135	0*	0	0	75	90**	80***

TABLE 6

15 POSTEMERGENCE HERBICIDE ACTIVITY  
OF OXATHIAZINES AT 6000 PPM

		PERCENT WEED CONTROL					
		PIGWEE OR VELVETLEAF*	JIMSON WEED	MORNING GLORY	BARNYARD GRASS	CRABGRASS OR SWITCH- GRASS**	GIANT OR GREEN*** FOXTAIL
20	COMPOUND						
	1	100	90	5	95	100	100
	3	100	35	65	100	85	100
	5	100	100	100	100	100	100
	6	100	100	30	100	100	100
25	7	0	0	5	10	5	5
	8	100	100	90	100	100	100
	9	100	10	98	100	100	100
	10	100	0	20	95	95	95
	11	100	5	35	35	50	75
30	12	50	0	10	25	10	0
	13	100	0	10	15	0	0
	15	100	50	98	95	80	30
	16	20	5	10	20	25	15
	17	25	5	10	10	5	5
35	18	100	20	45	90	75	50

TABLE 6  
(cont'd)  
POSTEMERGENCE HERBICIDE ACTIVITY  
OF OXATHIAZINES AT 6000 PPM

5	COMPOUND	PERCENT WEED CONTROL					
		PIGWEEED OR VELVETLEAF*	JIMSON WEED	MORNING GLORY	BARNYARD GRASS	CRABGRASS OR SWITCH- GRASS**	GIANT OR GREEN*** FOXTAIL
10	19	65	10	35	60	20	10
	20	0	0	0	10	0	0
	21	100	5	25	60	95	50
	24	100	100	100	95	75	45
	25	5	5	5	25	10	10
	26	100	100	70	98	98	95
15	27	100	5	15	98	100	98
	28	100	100	100	100	100	100***
	29	100	100	100	100	100	100***
	30	100	5	50	100	100	100***
	31	100	10	30	95	100	100***
	32	100	100	100	100	100	100***
20	33	100	100	100	95	100	100***
	34	100	0	5	90	75	90***
	35	100	10	85	70	50	50***
	36	100	0	5	70	95	95***
	37	100	0	0	55	25	25***
	38	100	90	75	80	80	90***
25	39	100	20	25	100	100	100***
	40	100	25	90	90	30	30***
	41	100	80	100	95	90	90***
	42	100	100	100	100	70	85***
	43	90	80	70	90	75	90***
	44	90	80	100	95	75	90***
30	45	100	20	30	90	95	100***
	46	80	65	75	60	40	25***
	47	100	10	45	75	75	90***
	48	100	0	5	80	75	100***
	49	95	0	10	25	10	35***
	50	50	0	5	5	-	5***

TABLE 6  
(cont'd)  
POSTEMERGENCE HERBICIDE ACTIVITY  
OF OXATHIAZINES AT 6000 PPM

5	PERCENT WEED CONTROL						
	COMPOUND	PIGWEEED OR VELVETLEAF*	JIMSON WEED	MORNING GLORY	BARNYARD GRASS	CRABGRASS OR SWITCH- GRASS**	GIANT OR GREEN*** FOXTAIL
10	51	100	0	5	5	-	15***
	52	100	0	30	25	-	50***
	54	-	50	5	100	100**	100***
	57	25	0	45	55	-	90***
	58	100	-	85	50	25**	80***
15	59	60	90	100	95	65**	95***
	60	0	0	0	20	0**	20***
	61	-	0	0	45	-	20***
	64	0*	0	0	5	0**	10***
	65	0*	0	0	10	0**	10***
20	67	0*	0	5	45	5**	35***
	68	0*	0	25	70	20**	80***
	69	0*	0	0	5	0**	10***
	70	0*	0	25	95	0**	95***
	71	100*	0	20	100	0**	95***
25	72	25*	0	55	75	0**	40***
	73	100*	100	100	100	10**	95***
	74	0*	0	0	15	0**	10***
	75	10*	0	10	80	0**	65***
	76	5*	0	25	50	0**	45***
30	77	0*	0	20	30	5**	10***
	78	0*	0	50	80	30**	90***
	79	0*	0	0	10	-	-
	80	0*	0	5	75	-	-
	81	0*	0	5	0	-	-
35	82	25*	25	75	80	-	-
	83	65*	25	75	95	-	-
	84	50*	25	60	100	-	-
	85	0*	0	35	90	-	-
	86	75*	20	75	100	-	-

TABLE 6  
(cont'd)  
POSTEMERGENCE HERBICIDE ACTIVITY  
OF OXATHIAZINES AT 6000 PPM

5	COMPOUND	PERCENT WEED CONTROL					
		PIGWEEED OR VELVETLEAF*	JIMSON WEED	MORNING GLORY	BARNYARD GRASS	CRABGRASS OR SWITCH- GRASS**	GIANT OR GREEN*** FOXTAIL
	87	100*	0	30	95	-	-
10	89	40*	0	0	35	0**	75***
	90	0*	0	75	80	90**	100***
	91	15*	0	85	65	5**	25***
	92	100*	90	85	100	100**	100***
	93	0*	0	5	15	0**	25***
15	96	5*	0	20	70	0**	30***
	97	5*	0	20	55	5**	40***
	98	0*	0	0	20	0**	25***
	99	0*	0	5	0	0**	0**
	101	10*	0	20	15	0**	15***
20	102	0*	0	5	0	0**	0***
	103	5*	0	15	30	0**	25***
	107	0*	0	5	15	0**	10***
	108	15*	0	40	60	5**	55***
	109	0*	0	0	0	0**	5***
25	110	15*	0	25	65	5**	100***
	111	0*	0	0	0	0**	5***
	112	0*	0	5	10	0**	10***
	113	100*	0	100	100	10**	100***
	114	0*	0	10	70	0**	100***
30	115	0*	0	0	10	0**	60***
	116	0*	0	5	40	15**	75***
	117	0*	0	0	5	0**	15***
	118	0*	0	0	40	0**	85***
	120	20*	15	45	5	0**	35***
35	121	5*	5	10	45	0**	55***
	122	10*	50	80	90	0**	100***
	123	0*	0	5	35	0**	45***
	124	0*	0	5	25	0**	75***

TABLE 6  
(cont'd)  
POSTEMERGENCE HERBICIDE ACTIVITY  
OF OXATHIAZINES AT 6000 PPM

5	PERCENT WEED CONTROL					
	COMPOUND	PIGWEEED OR VELVETLEAF*	JIMSON WEED	MORNING GLORY	BARNYARD GRASS	CRABGRASS OR SWITCH- GRASS** GIANT OR GREEN*** FOXTAIL
	125	15*	0	5	45	0** 35***
10	126	95*	5	35	25	55** 85***
	127	0*	0	15	0	- -
	129	50*	0	30	90	95** 75***
	130	90*	0	20	95	5** 75***
	132	100*	0	50	100	20** 70***
15	133	0*	0	20	80	5** 50***
	134	0*	0	30	75	0** 10***
	135	100*	0	15	95	85** 95***
	136	100*	85	100	100	70** 80***
	138	0*	0	0	10	9** 0***

- 20 Procedures for using the compounds of this invention as plant desiccants and defoliants may be in accordance with the state of the art in conventional agricultural practice. The active ingredient(s) may be included in one or more formulations suitable for use in conventional application equipment. Such formulations may be of
- 25 several different physical and chemical types, any of which could be made by anyone familiar with the art. For instance, the active ingredient(s) may be formulated into a soluble or emulsifiable concentrate that is prepared by dissolving the active ingredient(s) in one or more suitable solvents, such as acetone, toluene, or other
- 30 aliphatic or aromatic hydrocarbon, to which a dispersing agent has been added. Alternatively, the active ingredient(s) may be formulated as a wettable powder by grinding it into a fine powder and mixing it with an inactive powdered carrier, to which a dispersing agent has been added. Typical inactive powdered carriers include
- 35 attapulgite clay, vermiculite, talc, corn cob, activated carbon, mica and pyrophyllite. Alternatively, a wettable powder may be formulated by spraying a solution of the active ingredient(s) in organic

solvent onto the surface of an inactive powdered carrier as it is blended. The solvent is subsequently allowed to vaporize. The concentration of the active ingredient(s) in formulations of all types may vary widely, ranging from 0.1 to 95% active ingredient by weight.

Formulations bearing the active ingredient(s) may be dispersed in water and applied to target plants. Surface active agents may be added to the applied solution to increase its qualitative or quantitative range of activity. Suitable surface active agents are well known to those skilled in the art. Reference may be made to McCutcheon's Detergents and Emulsifiers (1980, Allured Publ. Co., Ridgewood, NJ) or to Hoffman et al in U.S. Patents 2,614,916 (cols. 2 to 4) and 2,574,724 (cols. 3 and 4) for examples of appropriate surface active agents.

The most suitable dosage of application of the active ingredient(s) and the type and amount of adjuvant substances to be added to the spray solution will depend on a number of factors, including the specific biological effect desired; the air and soil temperature; the quantity and intensity of rainfall before and after treatment; the soil type, pH, fertility and moisture content; the physiological condition and vigor of the target plants; the relative humidity and wind velocity of the air around the crop; the extent and density of the foliar canopy of the target plant; the light quality, intensity and duration each day; and the type and interval of previous and subsequent crop protectant chemical applications. All of these factors may have an influence on the efficacy of chemicals applied as harvest aids.

#### Example 20

To illustrate the effectiveness of the described oxathiazines as crop plant desiccants, a 6000 ppm solution/suspension of active ingredient was made up as described in Example 18. The chemical solutions/suspensions were applied to soybean<sup>(1)</sup> and cotton<sup>(2)</sup>

---

(1) Glycine max (L.) Merr. cv. Williams

(2) Gossypium hirsutum (L.) cv. Stoneville 213

plants as in Example 19. After 3 weeks in the greenhouse, the plants were scored for leaf desiccation on a 0 to 100 scale, 0 being no damage and 100 being complete kill. A rating system suggested by Frans and Talbert (1977. Research Methods in Weed Science, 2nd edition, Southern Weed Science Society) was used as a guide. The data obtained appear in Table 7.

TABLE 7

FOLIAGE DESICCATION ON COTTON AND SOYBEAN AT 6000 PPM

	Compound			Compound		
	No.	% desiccation		No.	% desiccation	
		soybean	cotton		soybean	cotton
10	1	5	35	19	95	100
	3	100	100	21	100	98
	5	100	100	24	100	100
	6	95	100	26	100	100
15	7	40	0	27	100	100
	8	100	100	28	100	100
	9	100	100	29	100	100
	10	98	98	30	100	100
	11	100	100	31	100	50
20	12	5	50	32	100	100
	13	0	100	33	100	100
	14	35	0	34	65	30
	15	85	95	35	100	95
	16	98	100	36	100	40
25	17	40	15	37	95	35
	18	98	98	38	100	85



TABLE 7 (cont'd.)

FOLIAGE DESICCATION ON COTTON AND SOYBEAN AT 6000 PPM

	Compound		<u>% desiccation</u>			Compound		<u>% desiccation</u>	
	No.		soybean	cotton		No.		soybean	cotton
5	39		100	100		75		90	0
	40		90	25		76		55	90
	41		100	100		77		65	0
	42		100	95		79		65	5
	43		85	20		80		85	5
10	44		90	100		81		65	0
	45		75	60		82		100	30
	46		95	100		83		100	90
	47		90	85		84		95	100
	48		30	15		85		80	15
15	49		30	20		86		100	65
	50		50	20		87		95	10
	51		15	80		89		95	100
	52		80	30		90		90	5
	54		30	10		91		95	100
20	57		90	5		92		95	100
	58		95	100		93		70	10
	59		95	0		96		95	100
	60		35	0		97		95	100
	61		80	0		98		25	0
25	64		25	0		101		75	30
	65		25	0		103		70	20
	57		90	5		104		25	15
	68		95	100		108		55	10
	69		45	0		110		65	5
30	71		95	95		111		55	0
	72		85	25		113		95	90
	73		100	95		114		30	0
	74		30	0		116		60	0

TABLE 7 (cont'd.)

## FOLIAGE DESICCATION ON COTTON AND SOYBEAN AT 6000 PPM

	Compound		% desiccation			Compound		% desiccation	
	No.		soybean	cotton		No.		soybean	cotton
5	118		20	0		130		100	100
	120		0	65		131		55	0
	121		35	5		132		95	100
	122		80	20		133		95	100
	124		25	0		134		85	10
10	125		20	5		135		95	100
	126		85	100		136		95	100
	128		0	25		137		35	0
	129		85	100		138		30	100

Example 21

- 15 To further illustrate the effectiveness of the described 3-aryl-5,6-dihydro-1,4,2-oxathiazines as plant defoliants, a 6000 ppm weight for volume (w/v) solution/suspension of tested chemical was prepared by dissolving 600 mg chemical in 10 ml suitable organic solvent. The solution was diluted to 100 ml with distilled water
- 20 containing about 2000 ppm w/v surface active agent (e.g., "Tween 20"). Twenty-five (25) ml of this 6000 ppm solution/suspension were diluted to 100 ml with distilled water containing about 2000 ppm surface active agent, resulting in a 1500 ppm solution/suspension of test chemical. The chemical was applied to cotton plants
- 25 (Gossypium hirsutum L. "Stoneville 213") by immersion of the lower leaves. At the time of treatment, the cotton plants had 2 to 4 true leaves. After treatment, the plants were returned to the greenhouse for about two weeks, at which time the plants were evaluated for defoliation of the treated leaves. The scoring system used: 1 =
- 30 5-25% defoliation, 2 = 26-50%, 3 = 51-70%, 4 = 71-85%, 5 = 86-100%. The results appear in TABLE 8.

TABLE 8

## COTTON DEFOLIATION AT 1500 PPM

	Compound No.	Defoliation Score		Compound No.	Defoliation Score
5	1	5	60	5	
	3	5		63	3
	5	5		64	5
	6	5		65	5
	9	5		66	1
10	10	5	67	67	4
	11	5		68	5
	12	5		69	1
	15	5		70	1
	16	2		71	2
15	17	5	72	72	3
	18	5		73	4
	20	5		74	1
	23	2		75	2
	24	5		76	5
20	26	5	77	77	2
	27	5		78	1
	28	5		82	2
	31	1		83	2
	33	3		84	5
25	35	5	86	86	1
	36	5		87	1
	37	4		88	1
	38	5		89	5
	39	2		91	5
30	41	5	92	92	5
	42	2		94	1
	44	3		95	2
	46	5		96	5
	51	3		97	5
35	52	5	100	100	1
	55	1		105	1

TABLE 8 (cont'd.)

## COTTON DEFOLIATION AT 1500 PPM

	Compound	Defoliation		Compound	Defoliation
	No.	Score		No.	Score
5	106	1		125	1
	108	1		126	5
	109	1		128	5
	110	1		129	5
	113	1		130	5
10	114	1		131	2
	115	4		132	5
	116	4		133	5
	117	2		134	5
	118	5		136	5
15	120	5		135	5
	121	2		137	2
	122	5		138	5
	124	2			

Similar defoliating activity is observed with compounds of this invention wherein R is trichlorophenyl, R<sup>1</sup> is n-butyl, t-butyl or benzyl and n is 0, 1 or 2.

In fungicidal applications, the chemicals may be applied directly to plants (i.e. seeds, foliage) or to soil in which plants are growing or to be grown, to protect against the harmful effects of pathogenic fungi. For example, the chemical may be applied to seeds by tumbling the chemical with the seeds, either alone or in admixture with a powdered solid carrier. Typical powdered solid carriers are the various mineral silicates, e.g., mica, talc, pyrophyllite, and clays. The chemical may also be applied to the seeds in admixture with a conventional surface-active wetting agent, with or without additional powdered solid carrier, as by first wetting the mixture with a small amount of water and then tumbling the seeds in the slurry. The surface-active wetting agents that may be used with the fungicide may be any of the conventional anionic, non-

ionic, or cationic surface-active agents. Such surface-active agents are well known and reference is made to U.S. Patent No. 2,546,724, columns 3 and 4, for detailed examples of the same. As a seed protectant, the amount of the chemical coated on the seeds will be 1/4 to 12 oz. (7-350 g) per hundred lbs. (45.5 kg) of the seed. As a soil treatment for fungi, the chemical may be applied: (a) as a dust in admixture with sand or soil a powdered solid carrier such as a mineral silicate, with or without an additional surface-active wetting agent, to the furrows simultaneously with the planting of the seeds; or (b) an aqueous spray, if desired including a surface-active or dispersing agent, or a surface-active or dispersing agent and a powdered solid carrier, to the seed rows before, or with, or after planting the seeds. As a soil treatment, the amount of the chemical applied to the seed rows will be from 0.1 to 10 pounds per acre (0.112 to 11.2 kg/ha) based on rows 2" (5 cm) wide and 2" (5 cm) deep a distance of 40" (102 cm) apart. Also, as a soil treatment, the chemical may be applied broadcast using a similar dust or aqueous spray with an application rate of 1.0 to 100 pounds per acre (1.12 to 112 kg/ha). As a foliage treatment, the chemical may be applied to growing plants at a rate of 1/4 to 10 pounds per acre (0.28 to 11.2 kg/ha). Such application is generally as an aqueous spray which also contains a surface-active or dispersing agent, with or without a powdered solid carrier or hydrocarbon solvent. These sprays usually are repeated at time intervals ranging from three days to two weeks during the growing season. Typical formulations are as follows (all percentages are by weight):

a) Emulsifiable concentrate:

30	48.1% Active Ingredient
	11.1% Surfactant (e.g., polyoxyethylene sorbitan monooleate)
	40.8% Xylene
	100.0% Total

## b) Wettable powder:

75.0% Active Ingredient  
2.0% Triton (trademark) X-120  
2.0% Daxad (trademark) - 11  
5      21.0% Dixie clay .  
100.0% Total

10 Triton X-120 is an alkylaryl polyether alcohol (9-10 moles polyethylene oxide) in dry powdered form (40% active on an insoluble carrier). The active ingredient in Triton X-120 is Triton X-100, which is a liquid nonionic surfactant (isooctyl-phenylpolyethoxyethanol, obtained by condensing the alkylphenylphenol with ethylene oxide). Daxad-11 is polymerized sodium salt of alkylnaphthalene sulfonic acid (more particularly, the sodium salts of binaphthyl/methane sulfonic acids obtained from naphthalene, sulfuric acid and 15 formaldehyde, according to U.S. Patent 1,336,759, Schmidt, April 13, 1920).

Example 22

Foliage Spray Treatment for Control of Established Bean Rust disease caused by the fungus (*Uromyces phaseoli*)

20      Although many chemicals will serve to protect plants from disease, it is often desirable to draw upon chemicals which have therapeutic properties to arrest the development of disease that has already become established. This example illustrates such properties.

25      Two hundred (200) milligrams of chemical were dissolved in 20 ml of acetone and 60 mg of a surfactant such as Triton X-100. This preparation was diluted with 80 ml distilled water giving a chemical suspension of 2000 ppm. Further serial dilutions were prepared from this as desired. The chemical suspensions were

30      sprayed on duplicate pots, each containing two snapbean plants which had, 48 hours prior to this, been inoculated with the bean rust fungus *Uromyces phaseoli typica* Arth. At the time of the chemical spray the bean plants had just begun to expand their first trifoliolate leaves. The test plants were then placed in a chamber

for 24 hours at 75°F (24°C) and 100% relative humidity. After this time the plants were returned to the greenhouse. About 10 days later the plants were scored for disease control, with the results shown in TABLE 9.

5 TABLE 9  
Bean Rust Disease Control by Foliar Application at 1000 ppm

	<u>COMPOUND</u>	<u>% DISEASE CONTROL</u>
	29	95
10	28	90*
	5	95

\* Some plant injury at this dosage.

Example 23

15 Foliar Spray for Protecting Tomato Plants from infection by the Early Blight Fungus, *Alternaria solani*

Test procedure:

One gram of the chemical to be tested was ground with three ml of acetone and 50 mg of a non-ionic surface-active agent (Triton X-100). The acetone and surface-active agent are known to be  
 20 inactive in this biological test. The mixture was diluted with water, giving suspensions containing 500 and 2000 ppm of the chemical. These suspensions were sprayed on duplicate six-inch (ca. 15 cm) tomato plants (variety Clark's Early Special) using a gun-type sprayer. Twenty-four hours later the treated and  
 25 untreated check plants were inoculated with a suspension of *Alternaria solani* spores by means of a 20 second spray from an atomizer sprayer (delivery rate 1 ml per second). The plants were then kept overnight in a controlled chamber at a temperature of 75°F (24°C) and 100% relative humidity. In the morning the plants  
 30 were transferred to the greenhouse. Three days later the disease was scored by comparing the number of disease lesions of the treated plants with the untreated control. The formula used to determine percent control is:

$$100 - \frac{(\text{Avg. no. lesions on treated plant})}{(\text{Avg. no. lesions on untreated plant})} \times 100 = \text{percent control}$$

The results are shown in TABLE 10.

TABLE 10

Control of Tomato Early Blight Disease  
by Foliar Application at 1000 ppm.

<u>COMPOUND</u>	<u>% DISEASE CONTROL</u>
4	92

10 Example 24

Foliar Spray for protecting plants from infection  
by the Rice Blast fungus, *Piricularia oryza*.

Test procedure:

The chemical suspensions were prepared in manner described  
in Example 23. The suspensions were sprayed on duplicate pots of  
clustered 7-day old barley plants (variety Herta) using a gun-type  
sprayer. The plants were then placed in a greenhouse together  
with untreated check plants and allowed to dry. All test plants  
were inoculated with the fungus by spraying with a suspension of  
*Piricularia oryzae* spores (20,000-40,000 spores/ml) to which a  
standard wetting agent has been added (Tween 20, 6 drops/300  
ml). After inoculation the plants were kept in a temperature-  
humidity control chamber for 24-48 hours at 70°F (21°C) to allow  
infection. Plants were then removed and placed in a 70°F (21°C)  
greenhouse to allow disease development. After 5 to 7 days, blast  
lesions appeared on the leaves. Disease control was evaluated by  
either counting lesions if infection was moderate or evaluating by a  
disease rating scale of 0-6 with 6 being severe disease. Percent  
control was computed by comparing the treatment scores with that  
of the untreated control (TABLE 11).



TABLE 11

Control of Piricularia Blast Disease  
On Barley by Foliar Application

	<u>COMPOUND</u>	<u>PPM</u>	<u>% DISEASE CONTROL</u>
5	32	1000	87
	4	500	84
	21	1000	83
	65	500	85
10	77	500	85
	91	500	100

Example 25

Antifungal activity as demonstrated by  
laboratory tests on fungus cultures.

15        The chemicals of the invention were dissolved in acetone, and  
applied at 500 ppm to 13 mm antibiotic testing discs by dipping the  
discs in the test solutions. After drying, the treated discs were  
placed on an agar plate (4 per plate), then 7 mm plugs of mycelium  
of various fungi were placed on the center of the discs in such  
20        fashion that the fungus mat was in direct contact with the treated  
disc. The fungitoxic activity of the chemicals was measured by  
comparing growth (colony radius) of the fungus on the treated  
discs with that on untreated controls. Colony radius was measured  
when untreated controls reached 80-90% of the area available for  
25        growth on the plates. The fungi tested were Alternaria solani (A),  
Fusarium oxysporum (F), Pythium sp. (P) and Sclerotium rolfsii  
(S). The results are shown in TABLE 12.

TABLE 12

	COMPOUND	% INHIBITION @ 500 ppm			
		A	F	P	S
5	6	65	-	90	-
	8	50	-	100	90
	9	50	-	100	-
	35	-	-	60	90
	47	70	-	-	-
10	48	70	-	-	-
	78	10	-	-	100
	29	75	70	100	30
	32	30	70	100	55
	41	80	-	100	80
15	42	80	-	100	80
	36	30	55	100	70
	28	85	70	100	40
	5	100	95	80	100
	19	95	90	100	95
20	46	95	95	100	80
	15	75	70	100	45
	52	100	-	100	65
	21	65	45	95	55
	33	100	100	100	95
25	38	75	65	100	100
	38	75	-	100	100
	53	100	-	100	65
	82	75	-	100	65
	84	80	-	100	65
30	86	100	-	100	85
	91	65	-	90	55
	43	-	-	100	55
	4	100	20	50	-
	59	80	-	-	40
35	7	20	-	100	50
	58	-	-	90	45
	17	80	70	30	30

TABLE 12 (cont'd.)

	COMPOUND	% INHIBITION @ 500 ppm			
		A	F	P	S
5	24	95	90	100	95
	21	45	5	85	25
	44	-	100	100	60
	53	90	-	60	50
	57	65	-	100	60
10	65	95	-	75	85
	77	75	-	80	60
	81	60	-	70	75
	85	90	-	100	65

Example 26

Foliar Spray for protecting plants from infection by the peanut  
 15 leafspot fungus, Cercospora arachidicola.

TEST PROCEDURE.

The chemical suspensions were prepared in a manner described  
 in Example 23. The suspensions were sprayed on duplicate pots of  
 clustered one-month old peanut plants (variety Florrunner), using a  
 20 gun-type sprayer. After the plants were dried, they were inocu-  
 lated with the fungus by spraying with a suspension of Cercospora  
arachidicola spores (20,000 spores/ml) to which a standard wetting  
 agent had been added (Tween 20, 6 drops/300 ml). Plants were  
 placed in temperature-humidity controlled chamber for 24-48 hours  
 25 at 70°F (21°C) to allow infection to be initiated. Plants were then  
 removed from the chamber and transferred to a 70°F (21°C) green-  
 house to allow disease development. After about 21 days, symptoms  
 had developed on the leaflets. Disease control was evaluated by  
 counting lesions if infection was moderate or evaluating by a disease  
 30 rating scale of 0-6, with 6 being severe disease. Percent control  
 was computed by comparing the treatment scores with that of the  
 untreated control. The results are shown in TABLE 13.

TABLE 13

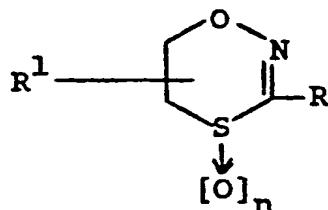
Control of Cercospora Leafspot Disease of  
Peanuts by Foliar Application

	<u>COMPOUND</u>	<u>PPM</u>	<u>% DISEASE CONTROL</u>
5	65	1000	95
		500	90
	77	1000	93
		500	95
10	84	1000	100
		500	100
	67	1000	80
		500	45
15	68	1000	85
		500	80
	72	1000	78
		500	78
20	73	1000	80
		500	75
	75	1000	50
		500	50
25	82	1000	90
		5000	80
	83	1000	90
		500	95
30	90	1000	96
		500	92
	95	1000	55
		5000	55
30	97	1000	80
		500	90

What is claimed is:

1. A compound of the formula:

5



wherein

10

$n = 0, 1 \text{ or } 2$

$R^1 = \text{hydrogen, } C_1\text{-}C_4 \text{ linear or branched alkyl or benzyl}$

$R = \text{phenyl or naphthyl}$

phenyl substituted with 1-2 of the following groups:

15

hydroxyl

halo

$C_1\text{-}C_{12}$  alkyl

$C_5\text{-}C_6$  cycloalkyl

trihalomethyl

phenyl

20

$C_1\text{-}C_5$  alkoxy or alkylthio

tetrahydropyranyloxy

phenoxy

$C_2\text{-}C_5$  alkylcarbonyl

phenylcarbonyl

25

$C_1\text{-}C_4$  alkylsulfinyl

$C_1\text{-}C_4$  alkylsulfonyl

carboxy or its alkali metal salt

$C_2\text{-}C_5$  alkoxycarbonyl

$C_2\text{-}C_5$  alkylaminocarbonyl

30

phenylaminocarbonyl

tolylaminocarbonyl

morpholinocarbonyl

amino

nitro

35

cyano

dioxolanyl

pyridinyl

thienyl provided n is 0 or 1

furanyl

furanyl substituted with 1-3 of the following groups:

5

$C_1-C_4$  alkyl

$C_2-C_5$  alkoxy carbonyl.

2. A compound as in claim 1 in which

$R^1$  = hydrogen or  $C_1-C_4$  linear or branched alkyl

R = phenyl;

10

phenyl substituted with 1-2 of the following groups:

F, Cl, Br except 2-Cl or 2,4- $Cl_2$  if n is 2

$C_1-C_4$  except p-t-alkyl if n is 0

$CF_3$

phenyl, except if n is 2

15

$C_1-C_5$  alkoxy

$C_2-C_5$  alkyl carbonyl

$C_2-C_5$  alkoxy carbonyl, except 4-alkoxy carbonyl if n

is 0

amino

20

nitro

cyano;

3- or 4-pyridinyl provided n is 0 or 1

thienyl provided n is 0 or 1

furanyl;

25

furanyl substituted with 1-3 of the following groups:

methyl

$C_2-C_3$  alkoxy carbonyl.

3. A compound as in claim 1 in which

$R^1$  = hydrogen or methyl

30

R = phenyl, provided n is 0 or 1

phenyl substituted with 1 or 2 of the following groups:

F, Cl, Br, except 2-Cl or 2,4- $Cl_2$  if n is 2

n- $C_1-C_4$  alkyl

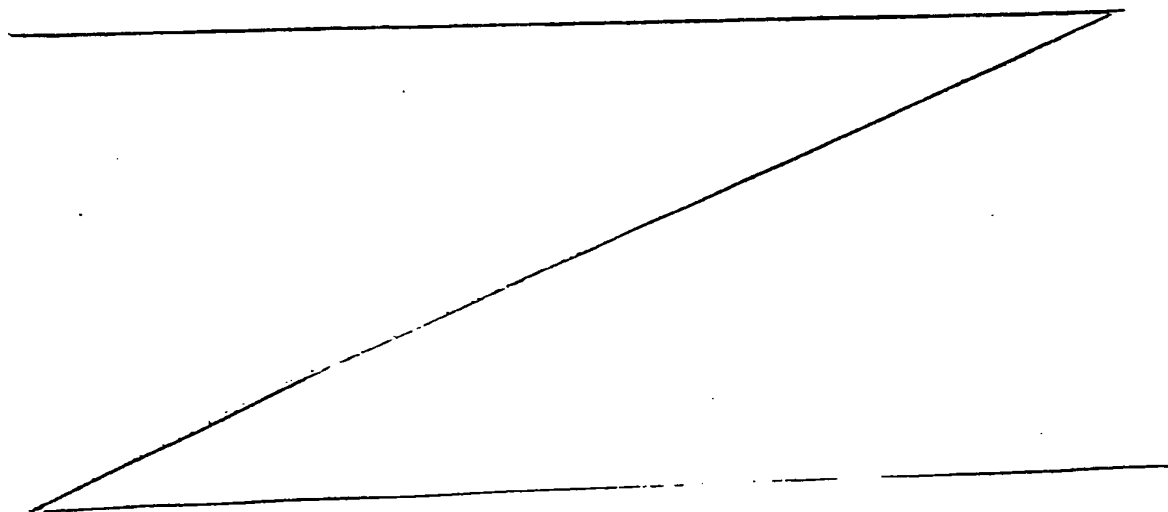
$CF_3$

- 5           C<sub>1</sub>-C<sub>2</sub> alkoxy  
          C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl, provided n is 1  
          C<sub>2</sub>-C<sub>3</sub> alkoxycarbonyl, provided n is 1 or 2  
          nitro  
          cyano;  
3- or 4-pyridinyl provided n is 0 or 1;  
thienyl provided n is 0 or 1;  
furanyl;  
furanyl substituted with 1-3 methyl groups provided n is  
10 1 or 2.

4. The compound of claim 1 wherein R<sup>1</sup> is hydrogen, n is 1 and R is phenyl, 3-fluorophenyl, 2-furanyl, 3,5-dichlorophenyl, 3-(methoxycarbonyl)phenyl or 4-chlorophenyl.

5. The compound of claim 1 wherein R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl or benzyl, n is 0, 1 or 2 and R is phenyl substituted with 3-Cl, 3-Br, 3-F, 2,5-dimethyl, 3-trifluoromethyl, 3-nitro or 3-cyano.

6. The compound of claim 5 wherein n is 1, R<sup>1</sup> is hydrogen n is 0 and R is 3-fluorophenyl.



7. A herbicidal, fungicidal, plant desiccant or plant defoliant composition comprising an effective amount of a compound as in claim 1 in admixture with a carrier therefor.

8. A method for controlling weeds comprising applying to a locus at which it is desired to control the weeds a herbicidally effective amount of a compound as in claim 1 in which R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl or benzyl; n is 0, 1 or 2; and

R = phenyl or naphthyl;

phenyl substituted with 1-2 of the following groups:

- 10 halogen except 2-Cl if n is 2
- C<sub>1</sub>-C<sub>12</sub> alkyl
- C<sub>5</sub>-C<sub>6</sub> cycloalkyl
- trihalomethyl
- C<sub>1</sub>-C<sub>8</sub> alkoxy except C<sub>4</sub>-C<sub>8</sub> alkoxy if n is 0 or 2
- 15 phenoxy
- tetrahydropyranyloxy
- C<sub>1</sub>-C<sub>8</sub> alkylthio
- C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl
- C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl
- 20 C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl provided n is 0 or 1
- carboxyl or its alkali metal salt
- 2- or 3-(C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl)
- C<sub>2</sub>-C<sub>5</sub> alkylaminocarbonyl
- 4-(C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl) provided n is 0 or 1
- 25 morpholinocarbonyl
- amino
- nitro
- cyano
- dioxolanyl;
- 30 4-pyridinyl provided n is 0 or 1;
- thienyl provided n is 0 or 1;
- furanyl;
- furanyl substituted with 1-3 of the following groups:
- C<sub>1</sub>-C<sub>4</sub> alkyl
- 35 C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl.



9. A method as in claim 8 in which  $R^1$  is hydrogen or  $C_1-C_4$  linear or branched alkyl and

if  $n = 0, 1$  or  $2$ ,

R = phenyl substituted with 1-2 of the following groups:

5

3- $CF_3$ ;

$n-C_1-C_4$  alkyl provided they are in 3- or 4-position;

3-pyridinyl;

furanyl

furanyl substituted with 1-3 of the following groups:

10

methyl

$C_2-C_3$  alkoxycarbonyl.

if  $n = 0$  or  $1$ ,

R = phenyl;

phenyl substituted with 1-2 of the following groups:

15

F or Cl

trifluoromethyl;

thienyl;

if  $n = 1$ ,

R = phenyl substituted with 1-2 of the following groups:

20

4-Br

$C_1-C_5$  alkoxy

3-nitro

4- $CF_3$

3-cyano.

25

10. A method as in claim 9, in which,

$R^1$  is hydrogen or methyl and

if  $n = 0, 1$  or  $2$ ,

R = phenyl substituted with 1-2 of the following groups:

4-Cl

30

3- or 4-( $n-C_1-C_3$  alkyl);

if  $n = 1$  or  $2$ ,

R = 2-furanyl;

if  $n = 1$ ,

R = phenyl;

35

phenyl substituted with 1-2 of the following groups:

3-Cl or 3-F

4-CF<sub>3</sub>

3-methoxy

3-nitro

5 4-(C<sub>1</sub>-C<sub>4</sub> alkyl);

2-thienyl;

if n = 0 or 1,

R = 3-pyridinyl;

if n = 0,

10 R = phenyl substituted with one of the following groups:

2,4-Cl<sub>2</sub>

2-Cl

3-Cl

4-F

15 2-Cl-6-F.

11. A method as in claim 8 in which the said compound has the structural formula of claim 1 and wherein R<sup>1</sup> is hydrogen, n is 1 and R is 3-phenyl, 3-fluorophenyl, or 2-furanyl.

12. A method for controlling fungi comprising applying to a locus at which it is desired to control the fungi a fungicidally effective amount of a compound as in claim 1 in which R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl or benzyl; n is 0, 1 or 2; and

R = phenyl or naphthyl

phenyl substituted with 1-2 of the following groups:

hydroxyl

halo



- C<sub>1</sub>-C<sub>12</sub> alkyl
- C<sub>5</sub>-C<sub>6</sub> cycloalkyl
- trihalomethyl
- phenyl
- 5 C<sub>1</sub>-C<sub>5</sub> alkoxy or alkylthio
- C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl
- phenylcarbonyl
- C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl
- C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl
- 10 carboxy or its alkali metal salt
- C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl
- C<sub>2</sub>-C<sub>5</sub> alkylaminocarbonyl
- phenylaminocarbonyl
- tolylaminocarbonyl
- 15 morpholinocarbonyl provided n is 1 or 2
- amino
- nitro
- cyano
- dioxolanyl
- 20 pyridinyl except 4-pyridinyl if n is 0
- thienyl provided n is 0 or 1
- furanyl
- furanyl substituted with 1-3 of the following groups:
- C<sub>1</sub>-C<sub>4</sub> alkyl
- 25 C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl

13. A method as in claim 19 in which R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl, and

if n = 0, 1 or 2,

R = phenyl or naphthyl

30 phenyl substituted with 1-2 groups:

F, Cl or Br in 3- or 4- positions;

if n = 1 or 2,

R = phenyl substituted with 1-2 groups:

C<sub>1</sub>-C<sub>4</sub> alkyl in the 3- or 4- position

35 3- or 4- trifluoromethyl

C<sub>1</sub>-C<sub>4</sub> alkoxy  
phenoxy  
C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl  
C<sub>2</sub>-C<sub>3</sub> alkoxycarbonyl  
5 nitro  
cyano;

if n = 1,

R = biphenyl  
3-cyanophenyl  
10 4-pyridinyl  
thienyl.

21. A method as in claim 20 in which,

R<sup>1</sup> = hydrogen or methyl

n = 1 or 2

15 R = phenyl

phenyl substituted with 1-2 of the following groups:

F or Cl

methyl

3-trifluoromethyl

20 3-methoxy

methylcarbonyl

3-methoxycarbonyl

4-methoxycarbonyl provided n is 1

4-ethoxycarbonyl

25 nitro

2-thienyl provided n is 1

2-furanyl.

14. A method as in claim 12 in which the said compound has  
the structural formula of claim 1 wherein R<sup>1</sup> is hydrogen, n is 1  
30 and R is 3,5-dichlorophenyl, 3-(methoxycarbonyl)phenyl, or  
4-chlorophenyl.

-60-

15 A method of desiccating plants comprising applying to the plants a desiccatingly effective amount of a compound as in claim 1 in which  $R^1$  is hydrogen,  $C_1-C_4$  linear or branched alkyl or benzyl and,

if  $n = 0, 1$  or  $2$ ,

R = phenyl or naphthyl;

phenyl substituted with 1-2 of the following groups:

Cl or Br in the 3-position

$C_1-C_{12}$  alkyl in the 3- or 4 position

3-trihalomethyl

$C_1-C_3$  alkoxy or alkylthio

$C_1-C_4$  alkylsulfinyl

$C_1-C_4$  alkylsulfonyl

carboxy or its alkali metal salt

3-methoxycarbonyl

4-ethoxycarbonyl

amino

cyano

dioxolanyl;

3-pyridinyl;

4-nitrotolyl;

furanyl;

furanyl substituted with 1-3 of the following groups:

$C_1-C_4$  alkyl

$C_2-C_5$  alkoxycarbonyl;

if  $n = 1$  or  $2$ ,

R = phenyl substituted with:

2-F or 4-Br

4-trihalophenyl

3-ethoxycarbonyl

4-methoxycarbonyl

4-nitro;

if n = 0 or 1,

R = phenyl substituted with

2-Cl

2-methyl

2,5-(CH<sub>3</sub>)<sub>2</sub>

C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl

morpholinocarbonyl;

4-pyridinyl;

thienyl;

if n = 0,

R = phenyl substituted with

3-F

2,6-Cl<sub>2</sub> or 2-Cl-6-F;

2-pyridinyl.

26. A method as in claim 25 in which,

R<sup>1</sup> is hydrogen, or C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl

if n = 0, 1 or 2,

R = phenyl;

phenyl substituted with

3-(Cl or Br)

3,4-Cl<sub>2</sub>

3-methoxy

3-CF<sub>3</sub>;

3-pyridinyl;

furanyl;

if n = 0 or 1,

R = phenyl substituted with:

2-(Cl or F)

3- or 4-(n-C<sub>1</sub>-C<sub>4</sub> alkyl)

2,5-(CH<sub>3</sub>)<sub>2</sub>

3-trifluoromethyl

3-methoxycarbonyl;

4-pyridinyl;

thienyl;

if n = 0,

- R = 2-tolyl;  
if n = 1 or 2,  
 R = 4-(trifluoromethyl)phenyl;  
if n = 1,  
 5 R = 3-nitrophenyl.

16. A method as in claim 15 in which the said compound has the structural formula of claim 1 wherein  $R^1$  is hydrogen or methyl, n is 0, 1 or 2 and R is phenyl substituted with 3-Cl, 3-Br, 3-F, 2,5-dimethyl, 3-trifluoromethyl, 3-nitro or 3-cyano.

- 10 17. A method as in claim 16 in which the said compound is the compound of claim 10 wherein n is 1,  $R^1$  is hydrogen and R is 3-fluorophenyl.

18. A method of defoliating plants comprising applying to the plants a defoliating amount of a compound as in claim 1 in which,

- 15 if n = 0, 1 or 2,  
 R = phenyl or naphthyl  
 phenyl substituted with 1-2 groups:  
 3- or 4-halo  
 3,5-Cl<sub>2</sub>  
 20 2-(C<sub>1</sub>-C<sub>4</sub> alkyl)  
 4-(C<sub>3</sub>-C<sub>4</sub> alkyl)  
 2,5-(CH<sub>3</sub>)<sub>2</sub>  
 phenyl  
 3-methoxy  
 25 4-(C<sub>2</sub>-C<sub>5</sub> alkoxy)  
 C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl  
 3- or 4-carboxy, alkali metal salt  
 3- or 4-methoxycarbonyl  
 C<sub>2</sub>-C<sub>5</sub> alkylaminocarbonyl  
 30 phenylaminocarbonyl  
 amino  
 3-nitro  
 3-cyano;

3- or 4-pyridinyl;

furanyl;

n = 0 or 1,

R = phenyl substituted with:

- 5                   2-halo
- 2,4-dihalo
- 2,5-(CH<sub>3</sub>)<sub>2</sub>
- 4-CF<sub>3</sub>
- 3-pentyloxy
- 10                  3-(C<sub>2</sub>-C<sub>3</sub> alkoxy carbonyl)
- morpholinocarbonyl;

thienyl;

n = 1 or 2,

R = phenyl substituted with:

- 15                  3-CF<sub>3</sub>
- 4-methoxy
- 4-nitro
- 4-nitrotolyl
- 3,4-Cl<sub>2</sub>;

20                  n = 0,

R = phenyl substituted with:

- 2-halo
- 3-methyl
- 3,5-(CH<sub>3</sub>)<sub>2</sub>
- 25                  phenoxy;

                  furanyl substituted with methyl and ethoxy carbonyl

n = 1,

R = phenyl substituted with:

- 2,6-Cl<sub>2</sub>
- 30                  4-CH<sub>3</sub>
- 4-ethoxycarbonyl;

n = 0 or 2,

phenyl substituted with tolylaminocarbonyl.

19. A method as in claim 18 in which R<sup>1</sup> is hydrogen or  
35 C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl



if n = 0, 1 or 2,

R = phenyl substituted with:

3-halo

3,5-Cl<sub>2</sub>

5

3-methoxy

4-carboxy alkali metal salt

3-amino

3-nitro

3-cyano;

10

3- or 4-pyridinyl;

if n = 0 or 1,

R = phenyl substituted with:

2-halo

4-(Br or Cl)

15

2,4-Cl<sub>2</sub>

2,5-(CH<sub>3</sub>)<sub>2</sub>;

2-thienyl

if n = 1 or 2,

R = phenyl substituted with:

20

3-CF<sub>3</sub>

3-CH<sub>3</sub>-4-NO<sub>2</sub>

4-nitro

4-methoxy;

if n = 0,

25

R = phenyl substituted with:

phenoxy;

if n = 1,

R = phenyl substituted with

C<sub>2</sub>-C<sub>4</sub> alkoxy

30

4-(C<sub>1</sub>-C<sub>4</sub> n-alkyl)

4-methylcarbonyl

3-(C<sub>2</sub>-C<sub>3</sub> alkoxy carbonyl)

4-methoxycarbonyl.

20. A method as in claim 18 in which the said compound is  
 35 the compound of claim 1 wherein R<sup>1</sup> is hydrogen or methyl, n is 0,  
 1 or 2 and R is phenyl substituted with 3-Cl, 3-Br, 3-F, 2,5-di-  
 methyl, 3-trifluoromethyl, 3-nitro or 3-cyano.

21. A method as in claim 18 in which the said compound is the compound of claim 10 wherein n is 1, R<sup>1</sup> is hydrogen and R is 3-fluorophenyl.

5 22. A method for making a compound as in claim 1 wherein R<sup>1</sup> is hydrogen comprising reacting a compound having the formula RC(=NOH)Cl with a compound having the formula ClCH<sub>2</sub>CH<sub>2</sub>SH, wherein R has the meanings as in claim 1.

23. A method for making a compound as in claim 1 comprising the steps

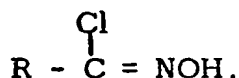
- 10 (1) reacting a compound of the formula RCS<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> with H<sub>2</sub>NOH, and
- (2) treating the equilibrium product of step 1 with a compound having the formula R<sup>1</sup>C(X)H-C(X)H<sub>2</sub> wherein R<sup>1</sup> hydrogen, C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl or benzyl in the presence of two equivalents of base.
- 15

24. A compound having the formula RC(=NOH)SCH<sub>2</sub>CH<sub>2</sub>Cl wherein R has the meanings as in claim 1.

20 25. A method of controlling weeds or fungi or regulating the growth of plants comprising applying to a locus, at which such control or regulation is desired, an effective amount of a compound as in claim 1.

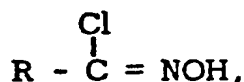
26. A method of making a compound as in claim 1 wherein n is zero, comprising contacting an N-hydroxycarboximidoyl chloride

25 of the formula



wherein R is as defined in claim 1, with 2-chloroethanol and a base, whereby a compound of claim 1 wherein n is zero is produced.

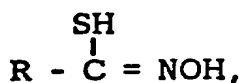
27. A method of making a compound as in claim 1 wherein n is zero, comprising contacting an aldehyde of the formula R - CHO wherein R is as defined in claim 1 with hydroxylamine to form the corresponding oxime of the formula R - CH = NOH, subsequently  
5 chlorinating said oxime to form the corresponding N-hydroxycarboxamidoyl chloride of the formula



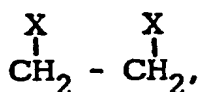
and thereafter contacting said N-hydroxycarboximidoyl chloride with  
10 2-chloroethanethiol and a base whereby the said compound of claim 1 wherein n is zero is produced.

28. A method as in claim 27 carried out in the presence of a solvent which is not changed in the successive steps of the process.

15 29. A method of making a compound of claim 1 wherein n is zero, comprising contacting an N-hydroxycarbimidothioic acid of the formula



20 wherein R is as defined in claim 1, with a vicinal dihaloalkane of the formula



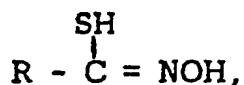
wherein X is halogen, and a base, whereby a compound of claim 1  
25 wherein n is zero is produced.

30. A method of making a compound as in claim 1 wherein n is zero, comprising contacting a carbodithioate ester of the formula R - CS<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, wherein R is as defined in claim 1, with hydroxylamine to form, with liberation of ethyl mercaptan, the corresponding N-hydroxythioamide of the formula

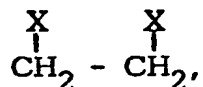


which enolizes to the corresponding N-hydroxycarbimidothioic acid

of the formula



and thereafter contacting said acid with a vicinal dihaloalkane of the  
5 formula



wherein X is halogen, and a base, whereby a compound of claim 1  
wherein n is zero is produced.

- 10 31. A method as in claim 30 carried out in the presence of a solvent which is not changed in the successive steps of the process.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0104940

Application number

EP 83 30 5783

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>2</sup> )
A, D	TETRAHEDRON LETTERS, no. 52, December 1972, pages 5267-5268, Pergamon Press, Oxford, GB S. HOFF et al.: "6-Acetamido-5,6-dihydro-1,4,2-oxathiazines: a novel class of compounds" * Pages 5267-5268 *  -----	1	C 07 D 291/06 C 07 D 419/04 C 07 D 419/10 A 01 N 43/88 G 07 C 153/00
			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>2</sup> )
			C 07 D 291/06 A 01 N 43/88
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-12-1983	Examiner CREMERS K.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**THIS PAGE BLANK (USPTO)**